

EXPERIMENTAL AND THEORETICAL
INVESTIGATION AND CHARACTERIZATION
OF SMALL MOLECULAR IONS

By

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by

Robert Lee Asher

I dedicate this dissertation to my parents and my wife. My parents' support and guidance started my education on the right footing. My wife encouraged me and was patient with me through the ordeal of writing this dissertation.

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The experimental work included in this dissertation would not have been possible without the help of the members of our research group, Philip Brucat, my principal advisor, and a previous graduate student Daniel Lessen, who taught me the ropes. The theoretical material was guided by David Micha as well as Dr. Brucat. Their experience helped me immeasurably.

Phil Brucat was for me scientific mentor, experimental motivator and friend. His genuine enthusiasm for the pursuit of scientific knowledge only slightly outweighed his enthusiasm for the pursuit of fun. From the first day in the lab, it was Phil who taught me that a chemist is really just a versatile plumber, electrician, machinist, and computer programmer, with a little chemical savvy and upper body strength. He frequently reminds me that the atoms in a system don't do any calculations; somehow they already know the answers.

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By

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May 1995

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Molecular ions have been generated via adiabatic supersonic expansion of a laser driven plasma. Ions within the resulting molecular beam have been collisionlessly mass selected so that ions of interest can be probed with tunable laser light. The photodissociation action spectra of these ions have revealed various details about both ground and excited states of the particular cluster ion.

Static and dynamic theoretical calculations, based upon pair potentials derived from experimental data, have been made for larger clusters. Simulated annealing calculations have determined the most likely structure of these clusters at 0 K. Classical dynamics calculations have dealt with isomerization rates, dynamic structure and vibrational analysis of the heterogeneous ion clusters.

CHAPTER 1 INTRODUCTION

The goal of chemists is to understand chemical interactions. These interactions are due to forces occurring on a molecular level. Thus, both experimental and theoretical physical chemists attempt to reveal the nature of these interactions by studying a small collection of atoms, which may in fact be part of a larger system. In this way, the larger system can be assembled by various workers taking one tractable system at a time. With this in mind, a detailed study of some cluster ions of the type $M_x(L)_y^+$ has been made, where M = a transition metal and L is a ligand such as a rare gas or small molecule. These small clusters have been chosen to model the chemically interesting parts of some larger systems such as solvation and catalysts. With the search for tractable model systems came the inevitable discovery of systems which are chemically interesting by themselves.

The experimental and theoretical modeling of cluster ions has been broken into separate sections in this dissertation. The goal, however, remains understanding how the forces between the atoms determine physically observable quantities.

Experimental Work

The experimental study of cluster ions has involved producing clusters, determining cluster identity, analyzing cluster spectra, and finally determining cluster properties from the spectra. Analysis of the spectra of most of the clusters that have been

observed requires that $x = y = 1$ or $x = 2, y = 0$. Cases where $x=1$ and $y \geq 2$ are of interest for conceptually step-wise solvation of an ion in the gas phase.

The bulk of the data presented in the following chapters deals with the vibrational energy levels built upon excited electronic states. These energy levels are probed with laser excitation and observed by photodissociation action spectra. This technique is powerful but limited, since the cluster must not only resonantly absorb light but must also fall apart in the time scale of the experiment. Other techniques, such as fluorescence and direct absorption are not practical for these systems because only small numbers of any particular ion can be produced. The vibrational data can yield a variety of information depending upon what is observed. If the vibrational dissociation limit is observed or predicted, the state can usually be assigned a term symbol. When naturally occurring isotopomers are available, the absolute vibrational numbering of an excited state can be made. If several vibrational progressions within a particular excited state are observed, then estimation of the spin orbit splitting can be made. When available, rotational energy levels provide information about the geometry of a cluster in both the probed excited state and the ground state. The cluster lifetime or other factors often limit the rotational resolution, however. Two-color experiments offer ways to determine excited state lifetimes. When used in combination with one-color spectra for comparison, they can elucidate bond dissociation energy from the onset of rapid predissociation in the resonant two-color dissociation (R2CD) spectrum as in the case of Ni_2^+ .

The systems presented in the resonant one-color dissociation (R1CD) sections include spectra of CoAr^+ , CoXe^+ , NiAr^+ , VXe^+ and ZrAr^+ diatomics. The CoAr^+ system

extends work which has been on going in the Brucat group. This is the first diatomic which has allowed full rotational analysis of numerous ro-vibronic bands and has vibrational progressions which correspond to the same electronic configuration in the transition metal ion. The CoXe^+ spectra are built upon the same Co^+ atomic states. The NiAr^+ spectrum is one of the first nickel-ligand cations with a resonant spectrum. Previous work in the Brucat group introduced a photodissociation edge, presumably due to a very short lifetime for the state. More recent investigation of NiAr^+ has revealed spin forbidden transitions, and allows for the determination of the diabatic binding energy of the ground state of the ion from three excited state limits. ZrAr^+ is another molecular ion which has been investigated in the past. Now, several excited states have been assigned as spin forbidden transitions, and the ground and excited state bond lengths have been determined. This is the heaviest diatomic to display rotationally resolved detail in this dissertation.

Several polyatomic systems, $\text{Co}(\text{H}_2\text{O})^+$, $\text{Co}(\text{CO}_2)^+$, $\text{Ni}(\text{H}_2\text{O})^+$ and $\text{Cr}(\text{H}_2\text{O})_6^+$ have given a great deal of insight into more complicated interactions which must occur as the number of atoms in the system increases. $\text{Co}(\text{H}_2\text{O})^+$ displays four electronic states, each with some rotational structure. $\text{Co}(\text{CO}_2)^+$ has bands built upon the same atomic ion states of the Co^+ that appear in CoAr^+ . It is probably the first spectrum of a linear polyatomic observed in the Brucat lab. $\text{Co}(\text{N}_2)^+$ undergoes a significant geometry change and yields an unusual photodissociation progression. The $\text{Ni}(\text{CO}_2)^+$ gives a sharp dissociation edge and leads to the ground state binding energy. $\text{Ni}(\text{H}_2\text{O})^+$ has the best rotational structure of the polyatomics in this dissertation. It offers the best chance for full analysis of a polyatomic

system. $\text{Cr}(\text{H}_2\text{O})_6^+$ has a nonresolvable spectrum. Its photofragmentation pattern at various photon energies has provided an approximation for the binding energy per water molecule.

Theoretical Work

In modeling clusters, an attempt has been made to determine properties which are physical, but which are not easily determined by current experiments. The hope is, of course, that eventually experiments will show that the approximate methods used for modeling have some predictive power.

The systems which have been modeled are the VAr_n^+ and CoAr_n^+ , in an attempt to gain understanding of solvation. Preliminary studies used simulated annealing, a zero degree Kelvin geometry optimization to determine the global potential energy minimum using various experimentally determined potentials. The resulting geometry conformations were analyzed to give static properties such as dipole moment, quadrupole moment, rotational constants and solvation shell closings.

More recent investigations have focused on dynamic properties of similar clusters. Classical trajectories have provided properties which include radial distribution functions, FFT power spectra of the $3N-6$ modes in the cluster and isomerization, isomerization rates and fitting the kinetic equations to the calculated data. Specific attention has been given to the VAr_6^+ system, which has two nearly isoenergetic isomers: the octahedral and capped tetrahedral. These have been of interest because the barrier to isomerization has

been found to be small and one geometry clearly dominates the phase space at non zero temperatures.

CHAPTER 2 EXPERIMENTAL

Several experimental setups have been utilized to obtain various types of data. The common goal in design of the apparatus has been the generation of a variety of internally cold gas-phase isolated cluster ions for photointerrogation. The difficulty in making these has been in obtaining correct conditions for their formation, which does not exclude the simultaneous functioning of numerous apparatus. The weak binding of the inductively bound species which are of interest precludes attempting normal methods of synthesis. In fact, the very species which must be routinely studied are thermodynamically unstable. This demands that the samples be made and interrogated within a short time period. To this end, the apparatus uses a variety of techniques to produce sufficient quantities of sample to obtain spectra.

Overview

A detailed outline of the majority of experimental equipment (manufacturers, dimensions, etc.) appeared previously.¹ However, sufficient additions and changes been made to warrant a revised detailed experimental section, which is provided here for completeness. See Figure 1 and the following discussion for a general overview of the experimental setup. A variety of $M_xL_y^+$ cluster ions are generated as a focused pulse of

Table I. Conditions for production of various ML^+ cluster ions.

Cluster Ion	Gas Mix % by volume Balance in He	Laser Power 532nm mJ/pulse	Backing Pressure PSI
$CoAr^+$	5% Ar	16	50
$NiAr^+$	5% Ar	18	70
$CaAr^+$	1.5% Ar	13	60
$CaAr^+$	< 1% Kr	10	70
CaN_2^+	5% N_2 + 3% Ne	10	60
$CoXe^+$	1% Xe + 10% Ne	16	70
VXe^+	1% Xe	16	50
$NiCO_2^+$	1% CO_2	16	40
$CoCO_2^+$	1% CO_2	15	30
NiH_2O^+	< 1% H_2O	18	40-80/40
CoH_2O^+	< 1% H_2O	15	50-100/30

532 nm light from a Nd^{+3} :YAG laser vaporizes the surface of a rotating transition-metal rod into high pressure helium pulse seeded with a small percent of the ligating gas (see Table I for conditions). The transition-metal cluster ions and neutrals are supersonically injected into a large vacuum chamber. The resulting adiabatic expansion robustly cools small clusters into the ground electronic state with little or no vibrational energy (to date no vibrational hot bands have been observed in our instrument). After traversing a differentially pumped section, the cations or anions are extracted at 90° into a two-stage

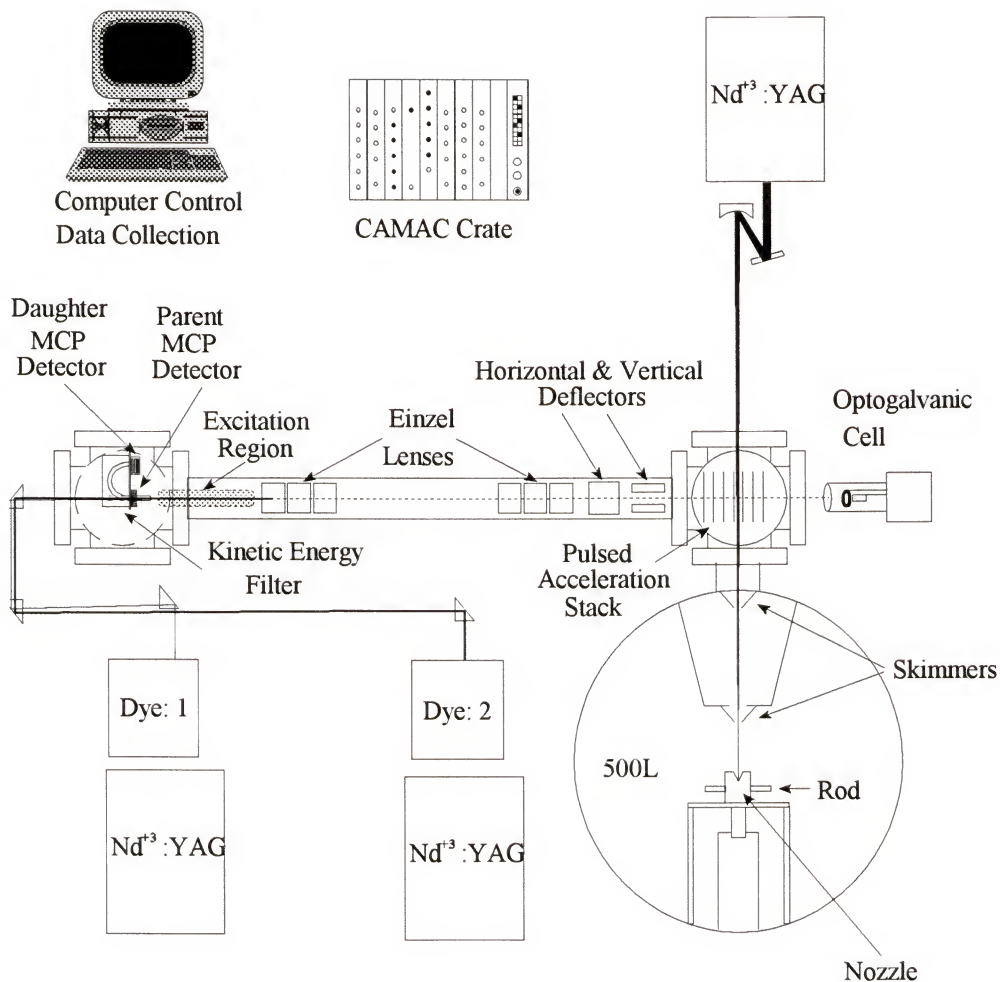


Figure 1. Experimental Apparatus.

The figure displays a schematic diagram of the experimental setup. A plasma is generated at the bottom of the figure in the nozzle, as a high pressure pulse of helium seeded with some atom/molecule. The vaporization laser comes through the mass spectrometer into the main chamber and creates the plasma at the surface of the rod. The plasma expands and cools. The beam traverses the main chamber and is then skimmed. The beam travels through a differentially pumped section and another skimmer orifice. The beam then enters the acceleration region of a custom time of flight mass spectrometer where the ions are extracted at 90° to the supersonic beam. The ions are accelerated to 1.45keV and deflected slightly to correct for their forward momentum. Mass separation occurs as the ions travel down the 2.45m flight tube which contains various deflecting and focusing optics. Fragment ions are detected at the daughter ion detector if they make it through the 180° hemispherical kinetic energy filter at the arrival time of the parent ions. Parent ions are monitored outside the entrance to the filter. Photodissociation action spectra are obtained by monitoring fragment ion current as a function of laser wavelength. Light passes through the mass spectrometer and strikes an optogalvanic cell for calibration.

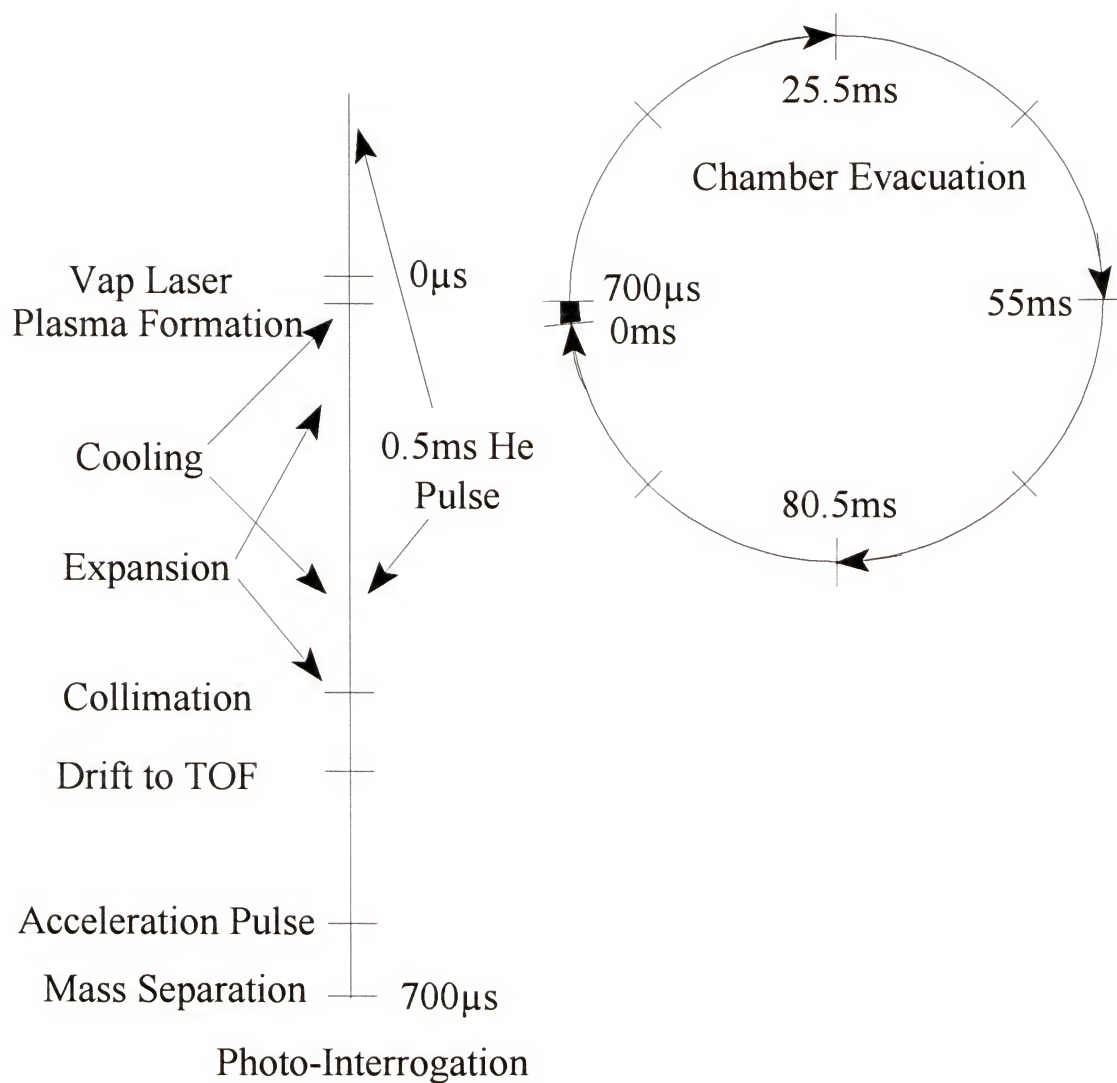


Figure 2. Experimental Cycle.

The figure shows a diagram of the experimental cycle. The experimental cycle is repeated at a frequency of 9.1Hz and the majority of the ca. 110ms is spent recovering from the helium pulse.

acceleration region of a custom time of flight mass spectrometer (TOFMS), where all the ions are accelerated to a kinetic energy of 1.45 keV. Ion optics guide the now spatially and temporally separated ion packets down a 2.45 m tube to the entrance slit of a 180° hemispherical kinetic energy analyzer. Ions which make it through this electrostatic sector are detected by a pair of microchannel plates.

The entire experiment is controlled by a CAMAC crate connected to a noname AT clone. The experimental cycle takes less than 1 ms and is repeated at 9.1 Hz.

Photodissociation action spectra are obtained by impinging a parent ion in the collimated ion beam with tunable light from a Nd⁺³:YAG pumped dye laser just prior to their entrance into the electrostatic sector. The electric field strength between the curved plates of electrostatic sector is adjusted to transmit daughter ions (ions which have either photofragmented or collisionally fragmented). The signal from the dual microchannel plates is amplified and collected by a signal averager. The fragment ion current is monitored as a function of the laser frequency and a sixteen shot average is collected to insure good signal to noise ratio. Spectral calibration of $\pm 1.5 \text{ cm}^{-1}$ is obtained by scanning the output of a capacitively coupled optogalvanic cell simultaneously.

Molecular Beam Generation

The experimental cycle (see Figure 2) begins with the helium pulse, which encompasses a rotating transition metal rod in a source block mounted on a removable flange inside the main chamber. The usual arrangement is a 6.35 mm rod mounted in a stainless steel block. The rod is captured by an O-ring, a Teflon spacer and a precision

bearing on both ends, as shown in **Figure 3**. The main chamber is evacuated by a NCR 10" and Varian 6" (model VHS-6) diffusion pump. Typical base pressure is 10^{-7} Torr while typical operating pressure is 10^{-5} Torr.

The helium pulse is made by over driving a commercial solenoid valve (General Valve series 9). A KEL-F_{TM} poppet seals the 0.76 mm diameter exit orifice of the valve in the de-energized state. The pulse is initiated by an amplified trigger pulse from a Kinetic Systems (model 3535) CAMAC module. The trigger pulse goes to a BNC pulse generator, which lengthens the trigger to the appropriate width. The TTL pulse drives a valve driver circuit containing a power Darlington MJ10016 which provides an electrical pulse of 150 V for 120 to 180 μ s. This pulls the ferrite back and delivers a gas pulse which is approximately 1ms in duration after delay. Backing pressure of 20 to 150 PSI delivers about 50 to 500 cm³ of gas into the chamber.

Within the helium carrier gas are the seeded atoms/molecules, which under the correct conditions will become bound to the transition-metal ions/neutrals. Two methods of seeding have been used to produce a variety of clusters. For gas phase atoms/molecules (such as Ar, Kr, Xe, N₂, SF₆...) tanks of a fixed concentration are prepared prior to an experimental run. Depending upon the desired concentration, this is done in one of three ways. For low concentrations (0.01% to 1.5%), an A1 cylinder (approximate volume 50 L) is placed on a custom high pressure manifold and evacuated to less than 1 mTorr. The tank is then closed off and the line is alternately flushed with helium and re-evacuated several times to insure no impurities can enter the tank. For percentages this low, the tank must have about one atmosphere of helium prior to adding

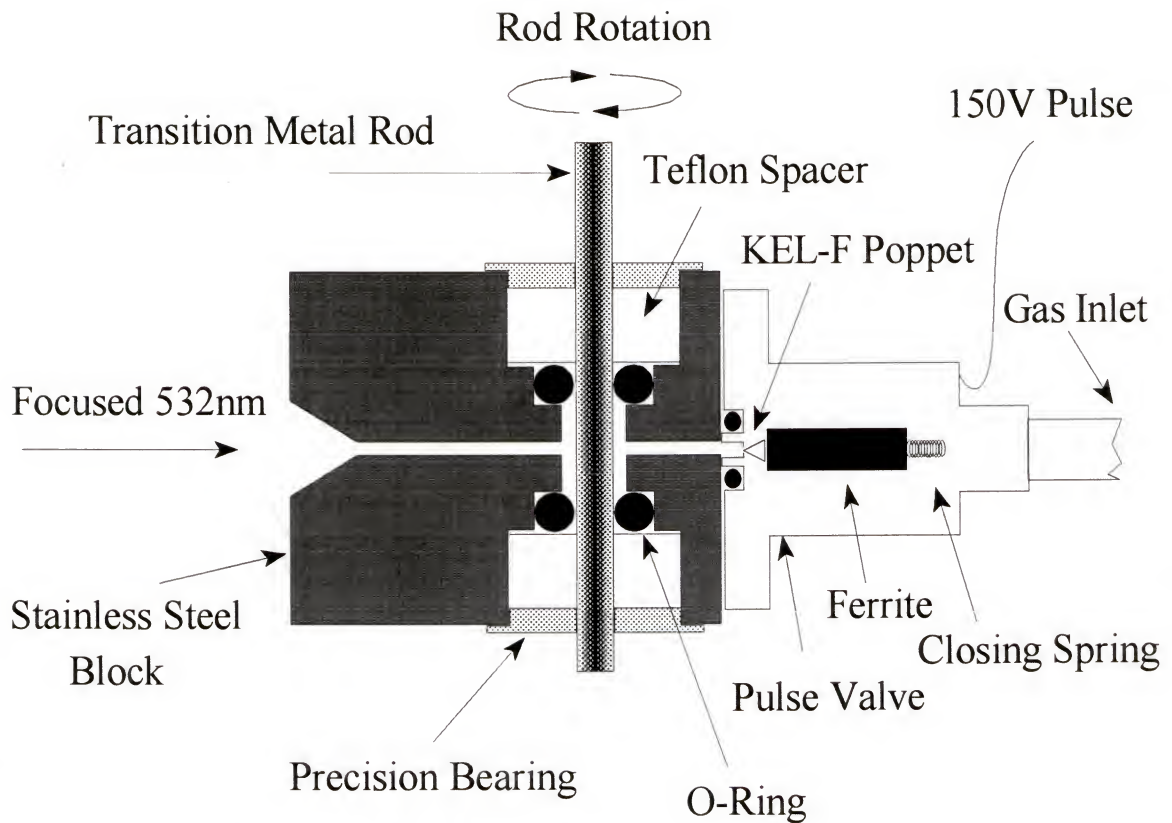


Figure 3. Source Block and Pulse Valve.

The figure displays the source block, transition metal rod and pulse valve. The poppet is forced open with a 120-180 μ s 150V pulse, which pulls the ferrite back. The focused laser pulse enters through the channel and vaporizes the transition metal rod in the center of the helium pulse. The rod rotates continuously to avoid cratering, which would deteriorate the signal level and the signal to noise ratio.

the seed gas, because most regulators read PSI relative to atmospheric pressure. The correct amount of seed gas is added to the tank with a standard two stage regulator, which can deliver ca. 150 PSI. The tank is then diluted to a total of 1000 PSI with a full A1 tank of helium (approximate 2500 PSI). For example, preparation of a 1% argon tank would require 10 PSI argon and diluted to 1000 PSI total. For concentrations which require a starting pressure greater than atmospheric pressure, the additional step of placing one atmosphere of helium into the tank first can be omitted. Instead, the value read just has one atmosphere added to it. Higher concentrations which would require more than the 150 PSI delivery pressure of a two stage regulator require a high pressure transfer. In this case a partially used helium tank can be directly added to from a full tank of seed gas on the high pressure manifold. Once the tank has had time to become thoroughly mixed (ca. one to two days) it can be used.

The mixing of liquid phase material into the gas beam has to be done dynamically. The main requirement to mix liquid phase material into the helium pulse is that the liquid have some vapor pressure at STP. The dynamic mixing is done in a custom manifold. The manifold is connected to a high pressure helium tank. The tank is regulated with a two stage regulator which can deliver up to 250 PSI. The liquid is contained in a reservoir which can be isolated on either side by two valves. After the reservoir, another two stage regulator can deliver 0 to 250 PSI of seeded gas. If the post-reservoir delivery pressure is the same as the pressure on the reservoir, this corresponds to merely blowing gas over the liquid, which yields the highest concentration possible. A second line bypasses the reservoir and allows for parallel delivery, which corresponds to the lowest concentration

possible. This is a very general description and will probably remain part of the black art of mixing. Many or even most of the liquids which are seeded into the beam react to some extent. This causes a change in arrival time at the acceleration stack, which precludes calculations of the exact concentration of the entrained liquid vapor.

The correct conditions for cluster formation are high pressure/density, correct concentration of the adduct atom/molecule and a coincident laser pulse. The laser pulse is focused using a 4, 5, or 6 m radius of curvature mirror which is approximately 2.2 m from the rod surface. The 532 nm light is 7 ns in duration with about 10 to 35 mJ/pulse produced by a Continuum (model Surelite II) Nd⁺³:YAG. The divergence of this laser and the focusing optics produce a point of light less than 1 mm in diameter. This gives a laser fluence of 10^8 to 10^9 W/cm² at the rod surface. With the above optics, this focus can be placed either behind, in front of or nearly on the surface of the rod. This adjustment is as important as the laser fluence and depends upon the metal which is being vaporized. Relatively soft metals like calcium are ablated best with the laser focus in front of the rod. Harder metals like nickel are best vaporized with the focus slightly behind the rod. Very hard metals like zirconium and molybdenum need to have the laser focused as close to the surface of the rod as possible.

The molecular beam passes through an electroformed 55° conical skimmer at 12 cm from the nozzle into a differentially pumped section. The differentially pumped section is actually a pie wedge section of the main chamber with a volume about 15% of the main chamber. This section is pumped by a Varian 6" (model VHS-6) diffusion pump with a chilled water cooled baffle, which achieves a base pressure of about 10^{-7} Torr and

an operational pressure of 10^{-6} Torr. The beam passes another 55° skimmer at 60 cm from the nozzle as it enters the "A" chamber of the mass spectrometer through a 7.62 cm gate valve, which can be used to isolate the mass spectrometer or main chamber.

The time of arrival at the "A" chamber can be used to determine a better measurement of the seed gas concentration from the following relationship:

$$t_u = t_{He} \sqrt{\frac{M_u}{M_{He}}} \quad (1)$$

where t_u is the unknown gas arrival time and M_u is the unknown average molecular weight. The arrival time depends upon the speed of sound of the carrier gas. As helium is diluted with seed gas, the average molecular weight and the time of arrival increases. The above relationship holds provided reactions in the source block channel do not quench the plasma rapidly or react explosively. The ions arriving in the "A" chamber are rapidly cooled in the expansion from the nozzle, and numerous methods can be used to calculate the ion temperatures. However, the best way to determine the temperature of the ions comes from fits to the rotational structure of their optical spectra, which will be discussed in Chapter 3.

Time of Flight Mass Selection

The molecular beam enters the acceleration region in the "A" chamber after about 1.1 m of travel in 600 to 700 μ s (depending upon the gas mixture used as discussed above). A rectangular packet of ions in the conical molecular beam is pulsed from the

acceleration region at 90° . The spread and composition of the conical beam is actually determined by the first skimmer diameter and the time at which the acceleration stack is pulsed. This "A" chamber is pumped by another Varian 6" diffusion pump with a liquid nitrogen cooled baffle, which can be gate valved off to isolate the mass spectrometer.

The initial spatial separation is diminished by a pulsed two stage Wiley-McLaren² acceleration with an adjustable high/low field ratio to focus various mass distributions at the detector. The first stage of the acceleration is a weaker field about 30 to 50 V/cm, while the second field is much larger, about 1440 to 1460 V/cm. The electrical pulse is produced by a Cober (model 605P) high voltage pulse generator which can deliver a 0 to 2 keV pulse of variable width and a risetime of ≤ 100 ns. The pulse is initiated by an amplified computer pulse from a Kinetic Systems 3535A CAMAC module.

The acceleration stack consists of parallel stainless steel plates (15.24 by 15.24 cm by 1.6 mm thick) separated by 1.0 cm Teflon insulating spacers. The plates have a central slot 2.54 cm by 7.62 cm to allow nearly collisionless passage. The first, sixth and seventh plates are grided with 90% open screen to keep the field in the two regions even. The first six plates which define the low field region are electrically connected by five $1.0 \text{ k}\Omega \pm 1\%$ tolerance glass resistors. The last, seventh, plate is grounded so the ions are in a field free region following the pulse. The potential on the sixth plate can be varied by a simple voltage divider. The ratio of the fields is determined by a ceramic high voltage switch with a series of discrete high voltage resistors which minimize the capacitance and therefore the ringing of the acceleration pulse.

As the ions leave the acceleration region, their forward momentum continues to carry them towards the wall of the TOFMS. They must be deflected by an adjustable static horizontal deflector -100 to $+100$ V/cm with a zero potential central plane.

Two einzel lenses are used to focus the ions into the entrance of the kinetic energy filter in the "B" chamber of the mass spectrometer. The "B" chamber is also pumped with a Varian 6" diffusion pump with liquid nitrogen cooled baffle and a gate valve to isolate the mass spectrometer.

Kinetic Energy / Mass Filtration

The apparatus initially used in this experiment had a 127° cylindrical electrostatic sector. This sector provided a wealth of data, but its throughput was only about 20%, which reduced the detection limits of the experiment. To increase the resolution and throughput, a 180° hemispherical sector was designed, shown in **Figure 4**. It has a 7.62 cm central diameter with 1.27 cm gap between the two spherical plates. The inner plate is a 3.175 cm radius aluminum hemisphere with flattened perpendicular edges cut 2.54 cm from center for mounting. The outer plate is a 4.445 cm radius hemisphere cut in relief in a 10.16 cm by 5.08 cm rectangular aluminum, also with perpendicular edges cut 2.54 cm from center. The side plates are oversized to allow mounting while avoiding touching the exposed charged surfaces. These plates are spaced off the two oppositely charged sections by 0.3175 cm ruby balls and are held in place by nylon screws. The face plate for the sector contains two detectors. The parent ion can be transmitted through the sector at when -460 and $+460$ V are applied to the inner and outer electrodes

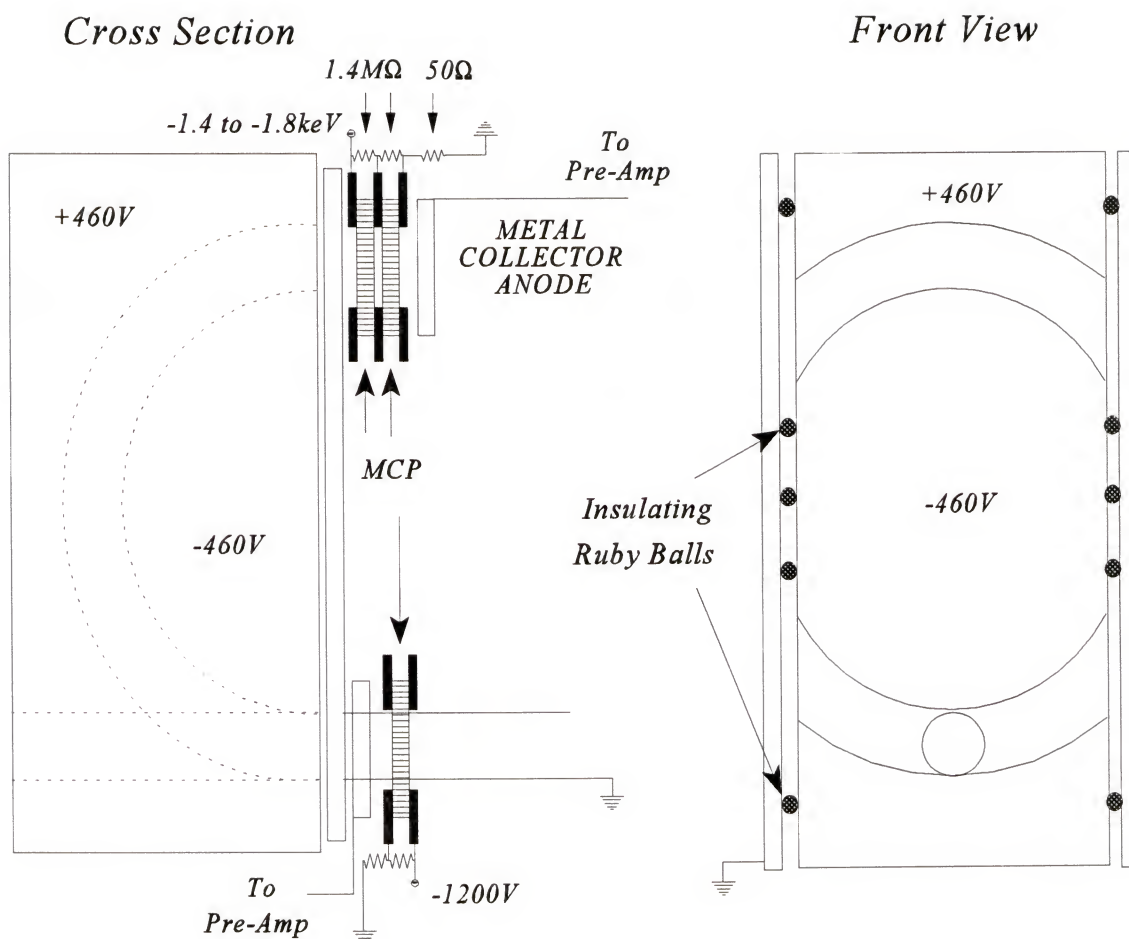


Figure 4. Hemispherical Sector and MCP Detector.

The figure shows a cross section of the hemispherical sector and microchannel plate (MCP) and a front view of the sector with front plate removed. The optimum voltage difference for this kinetic energy filter is 920 V for transmission of the parent ions having ca. 1450 V of kinetic energy. Fragment ions are filtered at a voltage approximately equal to the parent voltage times the fragment ion mass divided by the parent ion mass. (Velocity components in the backwards direction from photodissociation are relatively small compared to the initial velocity imparted by acceleration.)

respectively. This yields a radial electric field of about 725 V/cm. This hemispherical sector provides a secondary mass resolving power of about 75 at 100 amu. Daughter ions are transmitted at a proportionally smaller sector difference voltage. This improves sector transition to $\geq 50\%$ of the fragment ions, an improvement of at least 250% over the 127° cylindrical sector. The fragmentation of Co_9^+ , see **Figure 6**, with 532nm light (50 mJ/pulse) at a detector voltage of -1500 V gives some indication of the resolution and throughput of this sector. However, the best demonstration of the improvements is the observation of previously unobservable spin forbidden transitions discussed in the next chapter.

The parent ions can be detected nearly simultaneously (actually ca. 4.5 μs apart) with the daughter ions using these two detectors. The first detector is mounted around a central tube to allow parent or daughter ions through to the sector. This detector contains a single microchannel plate and signal plate. This Galileo microchannel plate can be biased to at least 1200 V. This detector allows primary mass resolving power of about 300 at 100 amu. It is surrounded by a grounded shield to avoid perturbing the ions trajectory. Ions which fall outside the tube are therefore detected as parent ion. The secondary mass ion detector is a dual microchannel plate detector which gives higher gain on the signal plate. This dual microchannel plate assembly uses two plates separated by a 0.127 mm nickel shim ring which makes electrical contact with the outer perimeter while leaving the detector area open. The shim acts as an electrical connection for a voltage divider. These two microchannel plates can be biased to 900 V each without breakdown. Incoming ions at this detector generate secondary electrons which are amplified by the second plate and

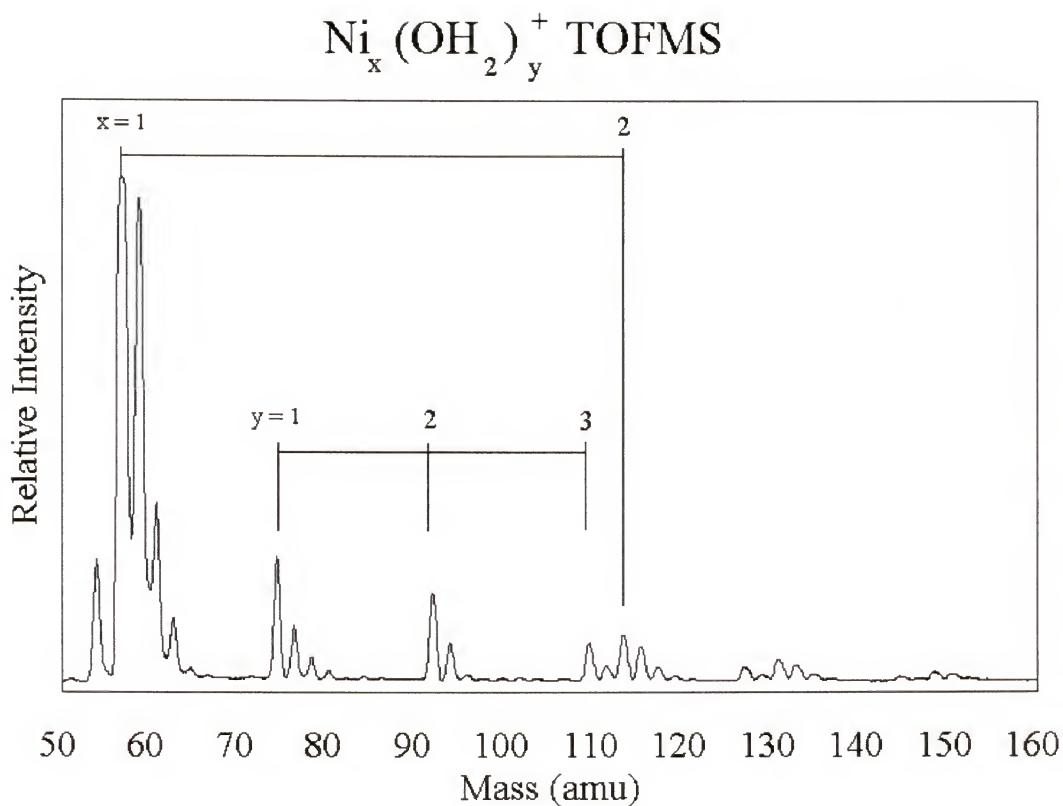


Figure 5. Time of Flight Mass Spectrum of $\text{Ni}_x(\text{OH}_2)_y^+$.

The figure shows time of flight mass spectrum of nickel cations complexing with water. Shown are only a small portion of the clusters which can be made. The horizontal deflector and acceleration stack ratio are optimized to give $\text{Ni}(\text{H}_2\text{O})^+$ with good isotopomer separation.

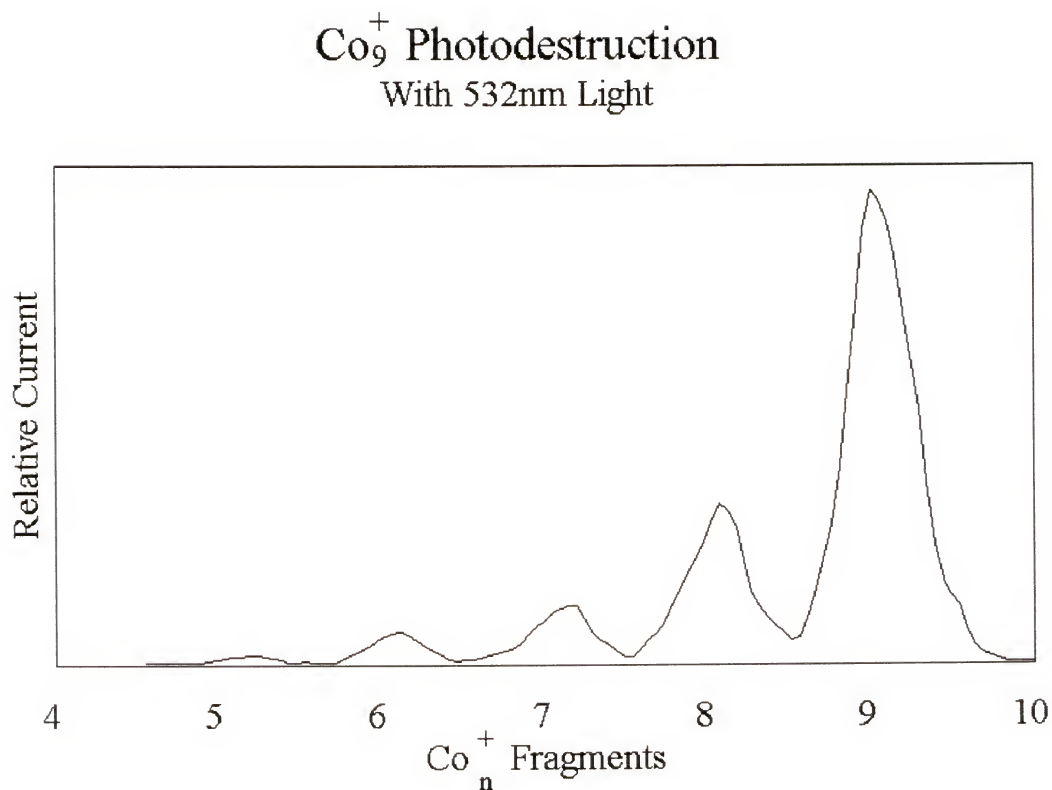


Figure 6. Photodestruction of Co_9^+ with 532 nm Light.

The figure shows the photodestruction of the Co_9^+ with 532 nm light. The plot is actually a internal scan of voltage on the sector and indicates that the Co_n^+ where $n = 5$ to 8 photoproducts are produced. The resolution of the sector is about 1 in 10 for the fragment ions, with good throughput.

finally onto a stainless steel electrode. The gain of this dual MCP is about 10^7 . This results in a time of flight mass spectrum (see **Figure 5**) which is taken 9.1 times a second. Correlation of ions which fall on the aperture and sector detector are shown in **Figure 7**. The correlation displayed is for single shot integration of the signal on each detector. The number of counts on the two detectors correlate along a predictable curve. For practical use, the signal on the aperture detector is used to simply monitor the parent ion during frequency scans, since these use a sixteen shot average to obtain a good signal to noise ratio.

Optimization of Cluster Formation

A great deal of time and effort are spent in producing a large and stable amount of the particular ion being investigated. Numerous groups have attempted to design a stable source for these weakly bound ions. It is not an easy task and the solutions for each new cluster ion may not be the same. In fact, besides the black art of mixing the right gas concentration, there are numerous variables which can lead to poor or unstable signal. Most of these difficulties reside in the inherently kinetic source.

Each time the experiment is run various parameters are changed, mainly due to human imprecision. The source block, which has been outlined previously, is the source of many of these changes. The transition metal rods which are used are near 0.635 cm in diameter. However, through use and variation from the manufacturer, the rod may develop some imperfection. Attempts to correct the imperfection have included polishing or even re-truing the rod. In either event the rod surface will degrade as the laser ablation

Detector Correlation Distribution

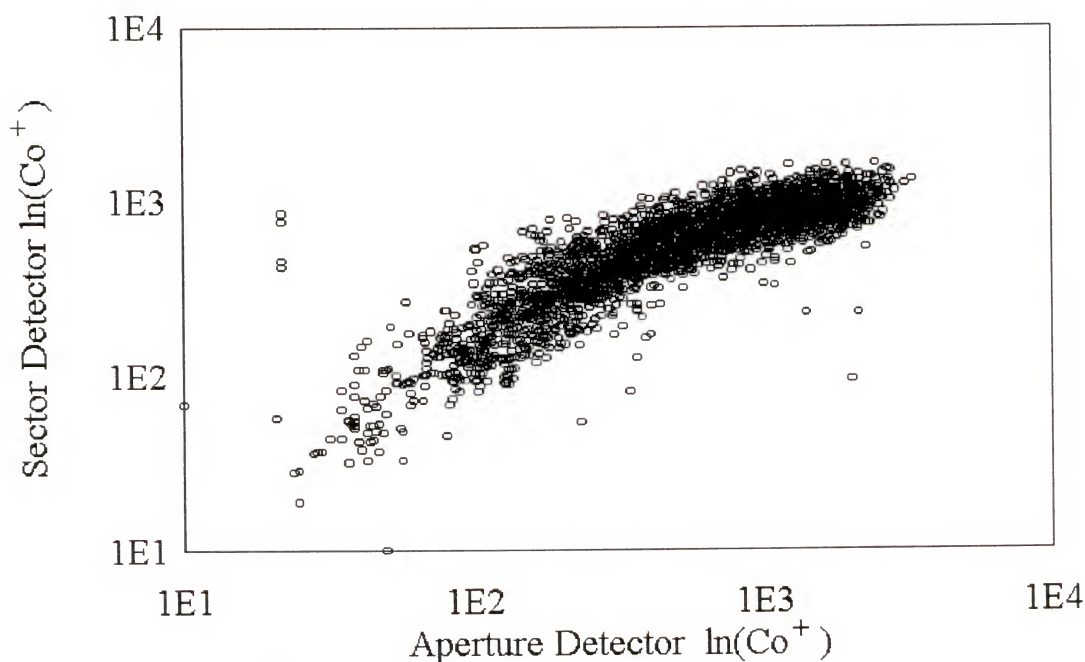


Figure 7. Correlation of Aperture and Sector Detector.

The figure shows correlation of the detection of Co^+ measured on the aperture and sector detectors. The number of counts on the aperture detector seem to correlate with the counts on the sector detector. Use of both detectors during a frequency scan should allow for the normalization of the spectrum to the amount of parent ion. In practice, however, this is slightly more difficult. The above picture is the correlation of single shots and frequency scans typically use a 16 shot average in order to obtain a good signal to noise ratio. In practice the signal from the aperture detector is simply monitored to insure that parent ion has not been lost.

progresses. There is an optimal point where the laser groove is just deep enough but not too deep. This condition may last for many hours over several days. Numerous factors can rapidly degrade the surface in an inhomogeneous manner. The O-rings are one key to the problem. Prior to each run, the O-rings are lubricated with a small amount of Teflon spray. The Teflon spacers press the O-rings into place such that the smallest amount of wear is incurred. The wear does occur, regardless of these precautions, and it occurs right where it can cause the most problems. If an O-ring fails in a particular spot where some sputtered plasma has accumulated, the wear can lead to an inhomogeneous rod surface. This type of leak is typically a cyclic occurrence and can clearly be seen in the production of parent ions. In fact, all periodic fluctuations in parent ion are directly related to rod rotation. Other sources of this periodic fluctuation in parent ion signal are related to misalignment of the rod in the block via incorrect coupling, which allows the rod to precess about the rotating axis.

Other sources of aperiodic fluctuations can come from the pulse valve. The pulse valve's KEL-F_{TM} poppet naturally degrades over time and eventually becomes leaky and erratic. Sometimes a particle of ablated metal can embed in the KEL-F_{TM} and cause erratic behavior from the start. Another source of instability can come from metal cluster build-up on the skimmers in the main and differential chambers. This build up occurs on the diffusion pump oil which "crawls around" from the unbaffled diffusion pumps in the main chamber. The skimmer thus becomes a capacitor which can charge and discharge irregularly. The ions encountering this charge are deflected out of the beam.

Most of the above problems can be avoided by regular maintenance. The remaining problems of finding the correct gas concentration, backing pressure, vaporization laser power, vaporization laser timing and acceleration pulse timing can be then be addressed in a somewhat systematic manner. Finally, the ion optics should be re-optimized to obtain the maximum amount of parent ion for each new cluster ion.

Optimization of one cluster often precludes the simultaneous production of large amounts of other clusters. Clusters of M_n^+ and ML_n^+ are formed under different optimal conditions and production of one can cause diminished amounts of the other. **Figure 8** displays this behavior to some extent. The increasing spread in dimer formation as the CoN_2^+ increases and the general decrease in CoN_2^+ make this an “anti-correlation”. This correlation is measured at the sector detector with integration of only single shots. Again, the practical use of this is only to help gain insight into the optimal production of various types of ions.

Optical Spectroscopy

Mass selection provides minimal information. True understanding of the cluster ion is gained from its photodissociation action spectrum. Therefore the mass selection is merely a prerequisite, which allows the determination of the spectrum of a particular cluster mass. Interatomic interactions are determined from the quantal details of the spectra obtained.

Tunable light is provided by a Quantel (model TDL50) or Lumonics (model 450) dye laser, which are pumped by a Nd^{+3} :YAG Quantel (model 581) or Continuum (model

Cluster Production Correlation

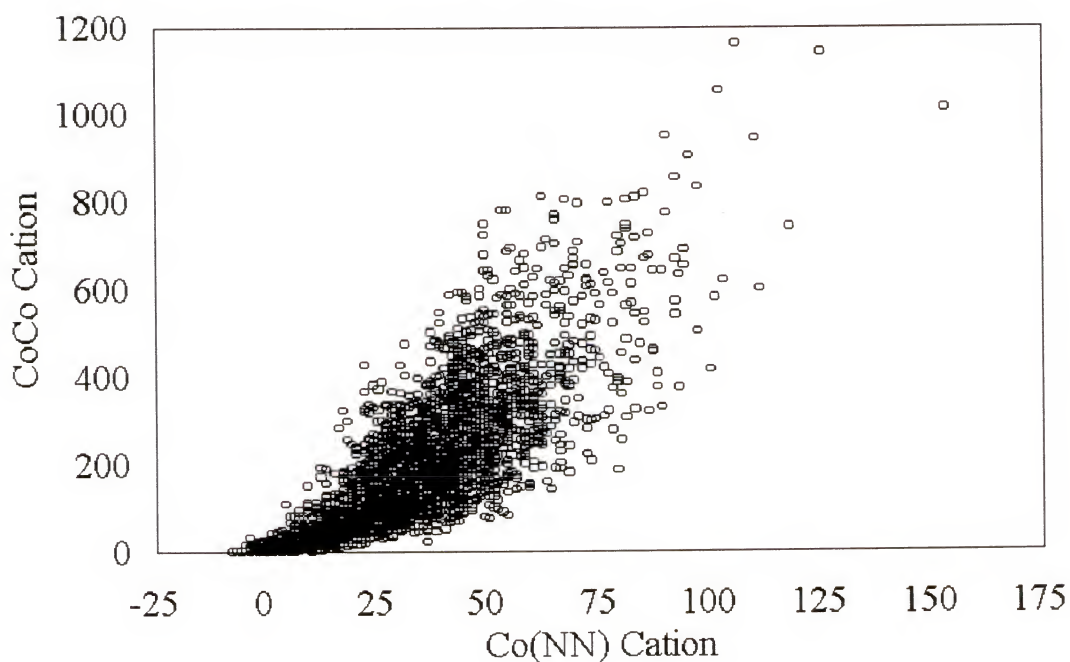


Figure 8. Correlation of Co_2^+ and $\text{Co}\cdot\text{N}_2^+$ production.

The figure shows correlation of the production of Co_2^+ versus CoN_2^+ measured on the sector detector. The dimer cation is formed with relative ease while the $\text{Co}\cdot\text{N}_2^+$ forms to a small extent. Additionally, as the spread in dimer formation increases as the $\text{Co}\cdot\text{N}_2^+$ increases. This spread and the decrease in CoN_2^+ formation in general make this an "anti-correlation".

Surlite II) respectively. The tunable light is timed to intersect the ion packet prior to the entrance of the electrostatic sector. These two YAG's can provide 1064, 532 or 355 nm light. The usual pump source is 532 nm, for most red dyes (fluorescein, rhodamine R590, R610, R640, DCM, LDS698, LD700, LDS765, LDS821, LDS865). 355 nm is used to pump blue dyes (coumarin C540A, C500, C440, C400). These provide about 5 to 50 mJ/pulse of light over a total range of 11200 to 25000 cm^{-1} relatively easily with only about dozen dye changes. Each dye has a near Gaussian power tuning curve which drops more steeply as it is tuned to the blue. The timing of the dye lasers is controlled by an amplified pulse from a LeCroy (model 4222) programmable delay generator that has ± 200 ps accuracy. The pulses control flash lamp charging, lamp firing and the Q-switch of the YAG.

Most of the spectra presented in this dissertation are composite spectra of multiple scans with various dyes and are overlapped where the dyes have similar power. The spectra are obtained in real time as the laser scans linearly in either wavelength or wavenumber. Ions which photodissociate come through the kinetic energy filter which is set to monitor daughter ions. The light continues through the mass spectrometer (indicated by the dashed line through the center of the TOFMS) and strikes an optogalvanic tube. The signal from the detector is amplified by a Pacific video amplifier (model 2A50) which gives a constant gain of 100 up to about 50 MHz. The capacitively coupled optogalvanic tube is amplified by a custom amplification circuit. The signals are digitized simultaneously by a DSP (model 2001S) transient digitizer and a LeCroy (model TR8837F) transient digitizer. This simultaneous scan optogalvanic tube with unknown

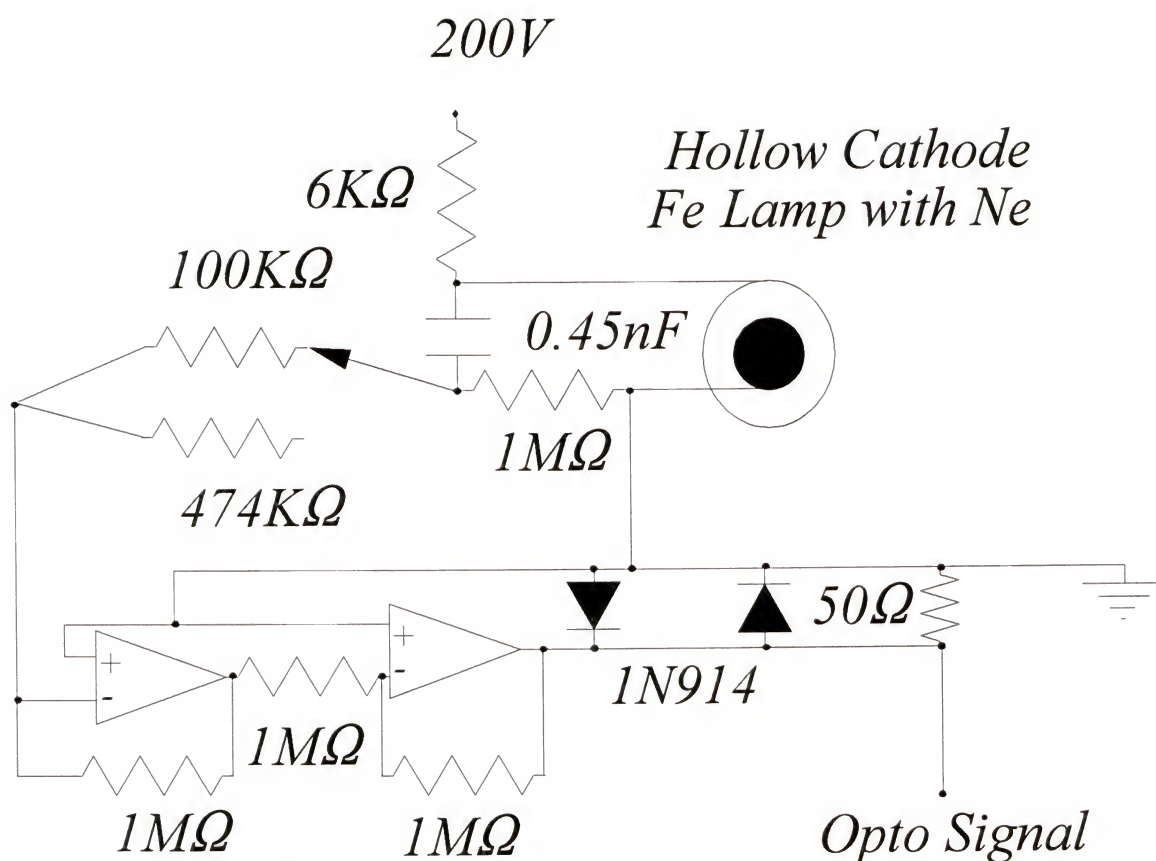


Figure 9. Optogalvanic Cell Diagram.

The figure shows the diagram of the optogalvanic cell and amplifier used in these experiments. The hollow cathode iron lamp contains neon gas. The lamp is run at 200 VDC and the output is capacitively coupled to the lamp. When the laser impinging the lamp hits a resonance, an inversion occurs, which causes a change in the current. The transition is amplified by a bifet amplifier (model TL082) and the output goes to a LeCroy waveform recorder (model TR8837F). The zener diodes prevent overvoltage reaching the waveform recorder.

Neon Optogalvanic Spectrum

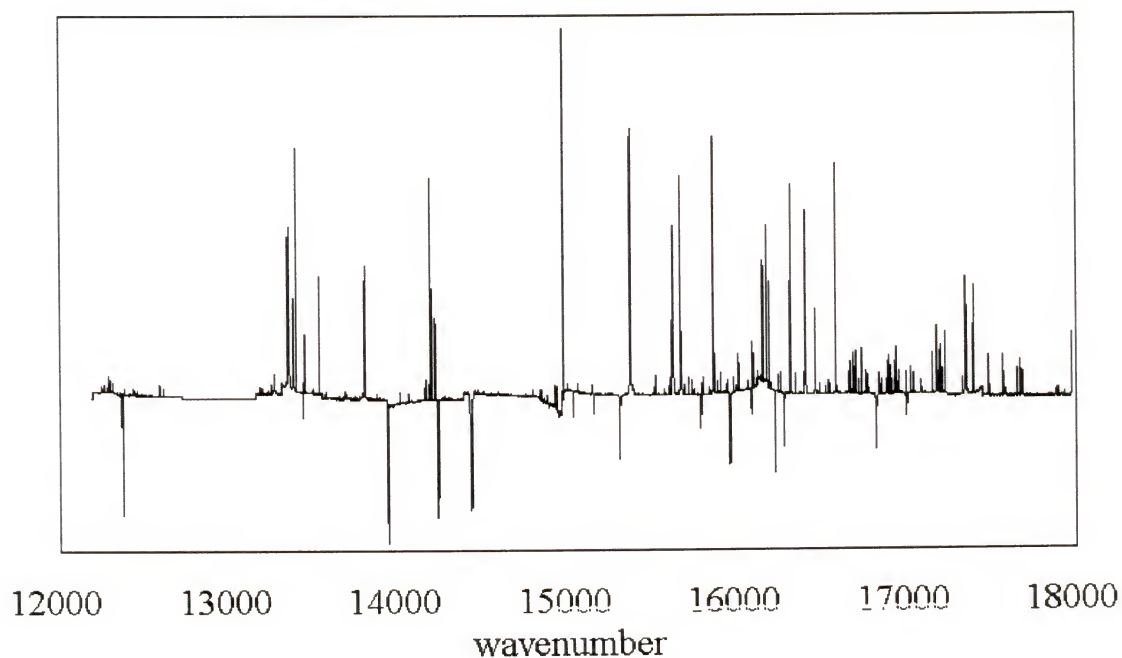


Figure 10. Optogalvanic Spectrum.

The figure shows a portion of the optogalvanic spectrum for neon from an iron hollow cathode schematically shown in **Figure 9**. The light passes through the mass spectrometer and strikes the tube. The photodissociation signal and optogalvanic signal are collected simultaneously. The line positions remain unchanged with each laser wavenumber scan. The intensity and sign of the signal, however, are variable. The intensity and sign depend upon probability of transition as is usually the case. Because the laser causes a population change of the neon atoms in the optogalvanic cell, the probability is also a function of the power of the laser light as well as the voltage applied to the hollow cathode.

spectra allows vacuum wavenumber correction to better than $\pm 0.5 \text{ cm}^{-1}$. The optogalvanic tube in use now has gone through several iterations and has become an invaluable part of the data workup. Figure 9 is a simple circuit diagram of the version which is now in use. Figure 10 shows the optogalvanic spectrum observed over the experimental dye range.

Typically, spectra are obtained co-linearly to the acceleration axis and thus the spectra must also be corrected for Doppler shift:

$$\nu_{corrected} = (1 + v/c)\nu_{observed} \quad (2)$$

where ν is the frequency of the light, v is the ion velocity and c is the speed of light. The velocity of the ions can be calculated with the following non-relativistic approximation:

$$v = 1.3891 \sqrt{\left(\frac{K}{m}\right)} \quad (3)$$

where K is the imparted kinetic energy in volts, m is the mass in amu and v is given in $\text{cm}/\mu\text{s}$.

Three types of photodissociation experiments have been performed in this apparatus without difficulty. These are shown schematically in the top two panels of Figure 11. The first is a typical one-color dissociation, where a photon excites an electron from the ground state electronic surface to an excited state. This type of absorption need not lead to dissociation, nor does it necessarily lead to a resonant

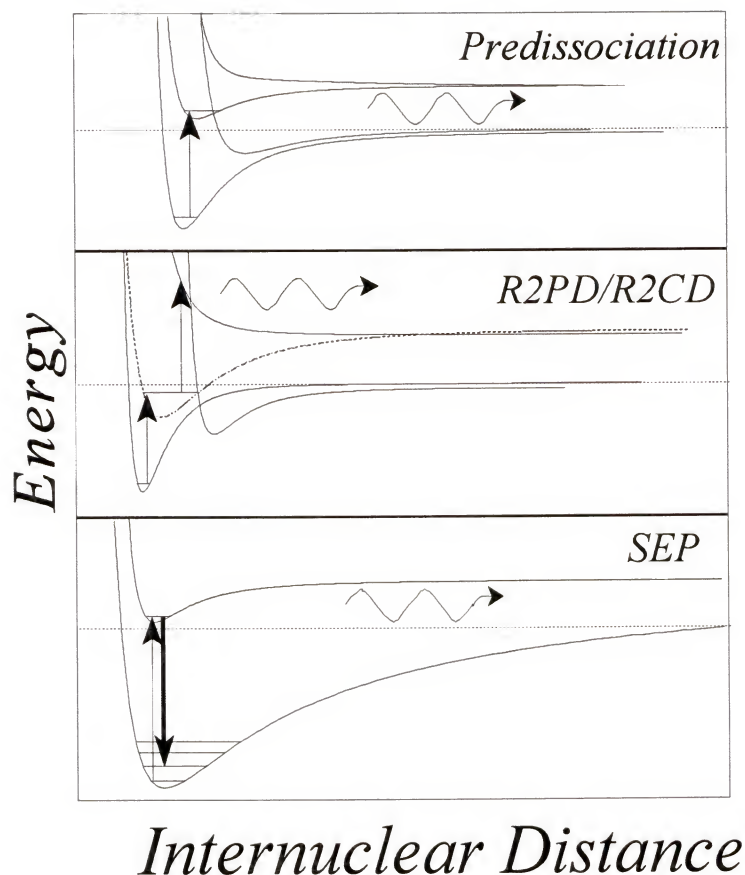


Figure 11. Four types of experiments which may be performed.

The figure shows the three types of experiments which have been performed with the current experimental setup. Predissociation is a one photon event where the photon is absorbed from the ground electronic state to an excited electronic state and subsequently undergoes dissociation. Resonant two photo dissociation (R2PD) undergoes the same first step but quickly absorbs another photon of the same energy to put the molecule in a dissociative continuum or a rapidly dissociating state. Resonant two-color dissociation (R2CD) is the same as R2PD except the second photon comes from another laser and can be a different color/energy. Stimulated emission pumping (SEP) is similar to R2CD in that the two photons come from different light sources but the second photon causes a decay back to the ground state. This final experiment has to date been unsuccessful due to difficulties in observing depletion of the dissociation signal.

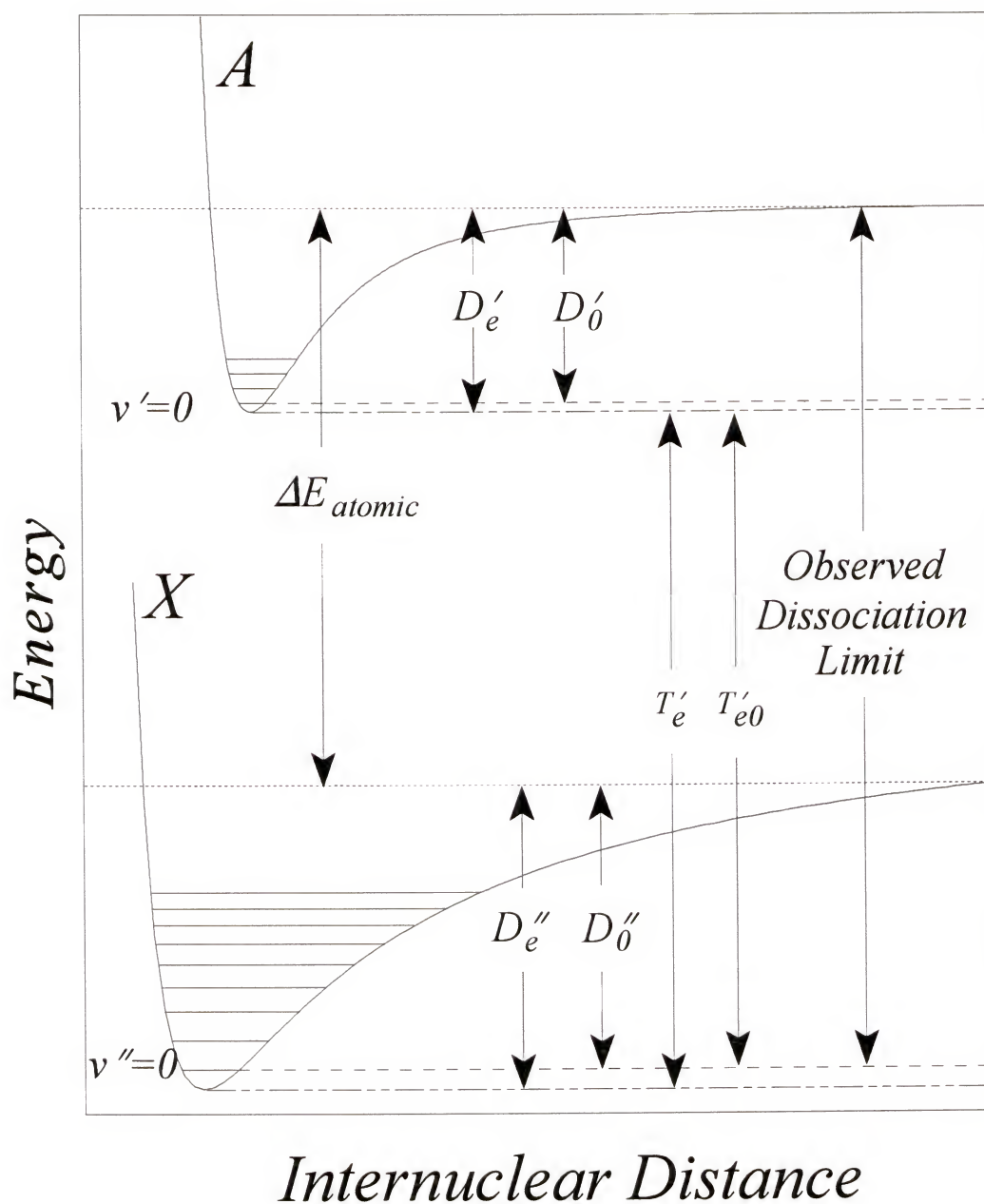


Figure 12. Electronic State Transition Explanations.

The figure displays the values used to describe the ground and excited electronic state and the separation between them. As the atoms go infinite internuclear distance they approach the atomic limits. Of particular interest is the fact that the ground state dissociation energy can be found from: $D_0'' = (D_0' + T_{e0}') - \Delta E_{\text{atomic}}$ and similarly $D_e'' = (D_e' + T_e') - \Delta E_{\text{atomic}}$. Given a molecule with several states for which dissociation limits have been observed and atomic separations are known, the ground state D_0'' can be determined, as it will be the constant in a system of equations.

dissociation. However, if coupling to a dissociative state after a resonant absorption occurs, a resonant dissociation spectrum is obtained. The second and third type of experiment involve the absorption of two consecutive photons followed by a dissociation event. The difference is resonant two-photon dissociation (R2PD) uses two of the same color photon (typically from the same laser pulse) and resonant two-color dissociation (R2CD) uses two photons which may be of different color (typically laser pulses from two different lasers). Each can give a resonant dissociation spectrum. The latter offers the possibility of determining the lifetime of the upper state and threshold for dissociation. A fourth type of experiment which may be performed, but as yet has not, is stimulated emission pumping (SEP). This involves two laser pulses of different color where the first photon excites and the second photon causes a decay back to the ground state before dissociation can occur. Typically, the first photon would be fixed to a known transition and the second photon would be tuned to obtain a photodissociation depletion, thus probing the ground electronic state. The next three chapters will deal with the electronic spectra of clusters. Several terms will be used to discuss these systems, displayed graphically in **Figure 12**. Most of these are commonplace terms and are only included here for completeness and to aid in the discussion which will follow.

After having shown how simple things appear, it must be mentioned that this is rarely the case. Even the simplest type of experiment which can be performed in the apparatus, resonant photodissociation, has proven nontrivial to obtain good spectra. A case in point is the power broadening of spectral features. This is a problem which was known to occur, but was not suspected to be very critical. The power which will broaden

features is not some fixed value and must be found experimentally for each molecule. An example is shown in **Figure 13**, where the two traces are of the same molecular ion CoAr^+ , with different amounts of laser power. The upper trace is power broadened. The vibrational information here is intact, but the rotational information has nearly been obscured. In extreme cases, background dissociation from excess power can eliminate even vibrational details. This is the case for particularly weak transitions such as spin forbidden transitions which have been observed in NiAr^+ and ZrAr^+ .

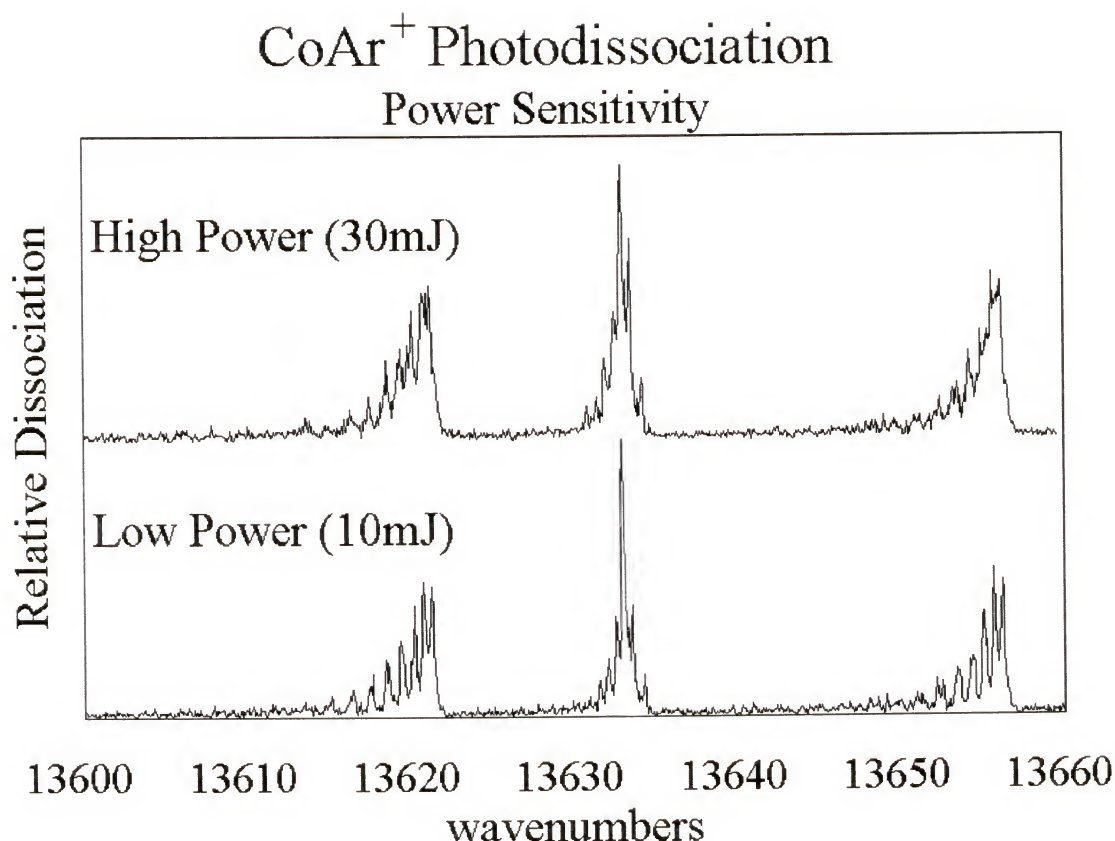


Figure 13. Power broadening of rotational structure in CoAr⁺.

The figure shows two traces of the CoAr⁺ photodissociation spectrum in the region from 13600 to 13660 cm⁻¹. Both traces are the relative Co⁺ current from CoAr⁺. The top trace is the result with about 30 mJ/pulse and the bottom trace is from CoAr⁺ with about 10 mJ/pulse across the same region. The upper trace was clearly power broadened with respect to the resolution obtained for the lower trace. Power broadening is an additional problem which must be solved in order to obtain the best spectra possible. With only the upper trace the rotational detail is nearly lost; in the lower trace it can be fully analyzed.

CHAPTER 3

ONE-COLOR PHOTODISSOCIATION OF DIATOMICS

The current experimental setup described in the previous chapter has allowed detailed analysis of numerous electrostatically bound systems and some more conventionally bound systems. High-resolution spectroscopy has characterized the chemical interactions between covalently bonded atoms since the beginning of this century³. The study of electronic, rotational and vibrational transitions in simple isolated molecules has provided quantum mechanical detail of the structure of the chemical bond. In fact, spectroscopic techniques grew along with the fundamentals of quantum theory. However, covalent bonds aren't the only interactions at work during a chemical reaction because, by necessity, the reactants are not isolated. The forces between non-bonded species are significant in all phases and become dominant in condensed phase. Yet, high-resolution spectroscopy works best in the gas phase where the species of interest is isolated and its energy levels are well defined. This is the motivation for making model compounds that exhibit the non-bonded interactions ubiquitous in condensed phases and yet which are tractable enough to be studied experimentally and theoretically to a worthy precision: 'clusters'. The spectra of weakly-bound van der Waals complexes or clusters, which exhibit the dispersion forces found in all liquids, have been made possible by the

application of supersonic beam techniques⁴ which allow these species to be studied in the same way that stable, chemically-bound species have suffered analysis.

When the non-bonded fragments of the liquid or cluster possess a net charge, the magnitude of the interaction is increased greatly relative to neutrals due to strong, long-range electrostatic and inductive forces that are a consequence of the non-vanishing electric monopole moment(s). This behavior is of great significance to the behavior of every electrolytic solution: consider the thermodynamics of a dissolution of a simple salt or the distribution of conformations of the biologically relevant polyelectrolytes we call proteins. The forces in these solutions are usually categorized by a multipole expansion of the static and polarized charge distributions of the fragments involved, as alluded to above. For example, a simple atomic ion interacting with a single water molecule is expected to exhibit mainly charge-dipole, charge-quadrupole, and charge-(induced-dipole) forces, although some higher-order terms are clearly non-zero. The details of such $M^+ \cdot (OH_2)$ interactions, as modeled by cluster spectroscopy, have recently been derived experimentally^{5,6} and theoretically⁷. But, in the spirit of simplification to its extreme, one might consider a model system that features only one dominant force due to the electric charge, i.e. a system that has a simpler 'solvent' than water. For that reason, and in analogy to the first neutral van der Waals systems studied in the gas phase, the focus in our group has been the interaction of an atomic ion with a rare-gas atom. The following sections consider the geometric structure of a $M^+ \cdot Rg$ diatomic complex in which only charge-(induced-dipole) binding forces dominate, where M is a transition-metal and Rg is a rare-gas. Many of these systems reveal only simple vibrational structure but a significant

CoAr⁺ Resonant Photodissociation

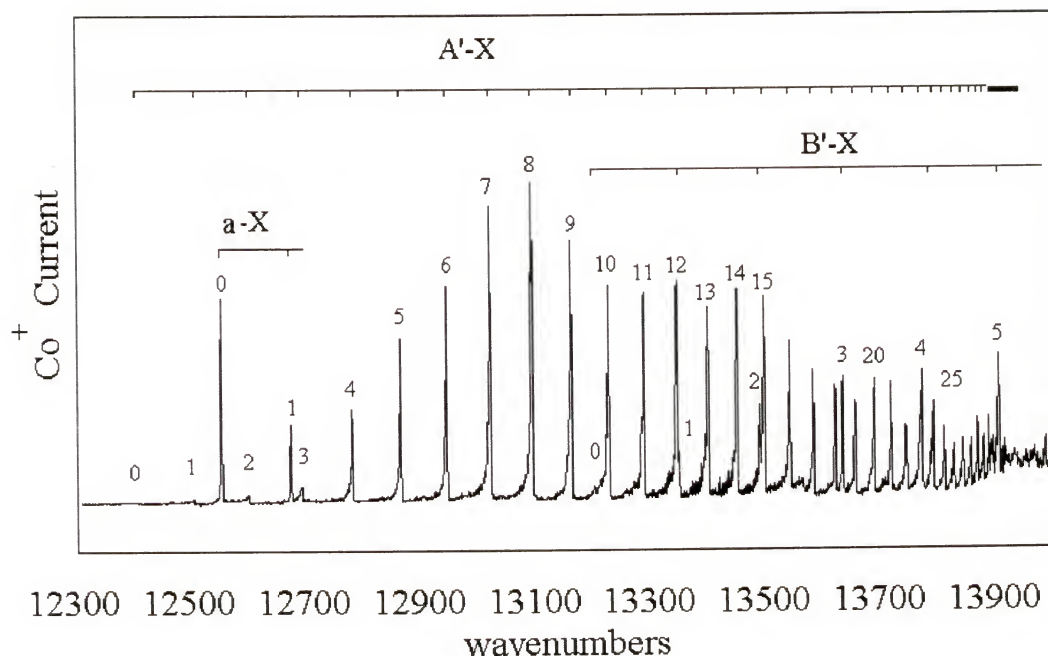


Figure 14. The CoAr⁺ a, A' and B' States.

The photodissociation excitation spectrum of CoAr⁺ observed in the frequency range of 12300 - 14000 cm⁻¹. The horizontal axis for all spectra is dissociation laser frequency in wavenumbers and the vertical axis is relative photofragmentation of mass selected CoAr⁺ to yield Co⁺. Three electronic transitions not previously observed for this molecular ion are observed and labeled in this figure. The a-X transitions near 12600 cm⁻¹ have been truncated as they are distorted by saturation in this scan.

few give rotational detail. It is this rotational detail which allows for bond length determination for both ground and excited electronic states.

Cobalt Argon Cation

The CoAr^+ diatomic has been investigated by our group previously.⁸ Three electronic states were probed from 14000 to 17500 cm^{-1} . These states were assigned by their dissociation limits. In this section the description of three new states and correction of the ground electronic state assignment will be described. Rotational detail of all of these states has made this assignment possible. Bauschlicher et al.⁹ calculate R_e , ω_e , and D_e for several excited states and the ground state of this system. These were found to be in disagreement with the experimentally determined values by about 20%.

The cobalt argon is produced in the manner described previously under conditions listed in Table I. The ion ensemble was intersected prior to the entrance of the 180° sector and the fragments were detected at the kinetic energy of the Co^+ fragments which arrive at the time of arrival of the CoAr^+ parent. The dissociation laser was tuned from 12000 to 14500 cm^{-1} , where the three new states were found.

Excited States of CoAr^+

The spectrum discussed here is to the red, lower energy, of that reported previously for the same molecule⁸ and contains three additional electronic transitions not previously observed. Figure 14 shows a portion of the photofragmentation excitation spectrum of the CoAr^+ ion showing the region of 12300 to 14000 cm^{-1} . The bands in three electronic transitions are labeled by their upper state vibrational quantum number

CoAr^+ A'-X (13,0) Transition

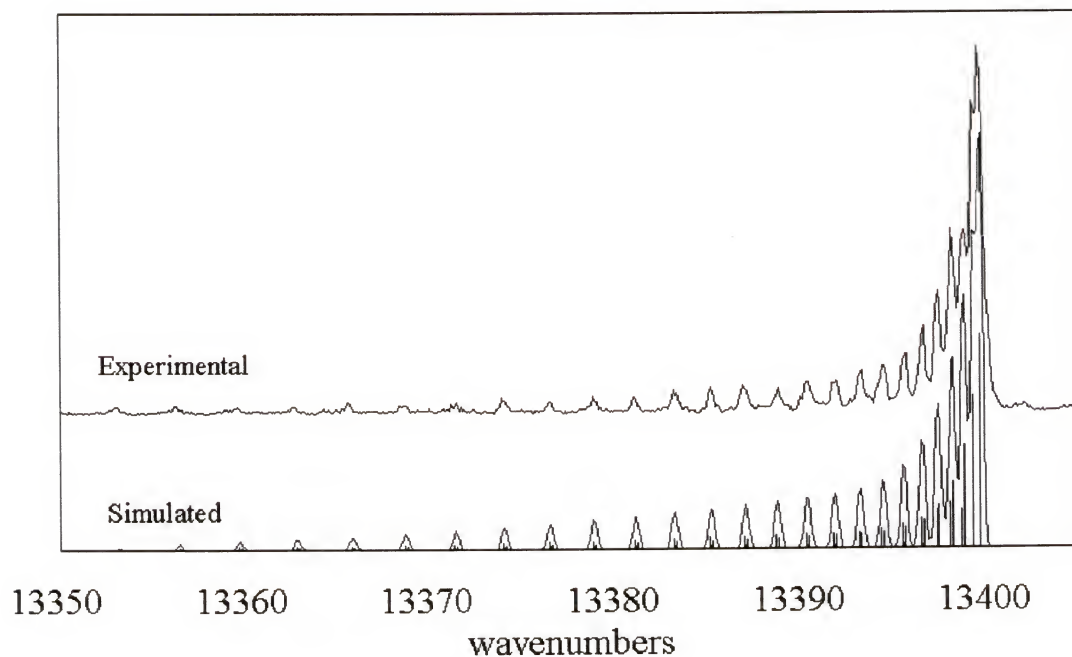


Figure 15. The CoAr^+ A'-X (13,0) Band.

The figure shows a closeup of the A'-X (13,0) band showing rotational structure. The upper trace is an experimental spectrum and the lower is a calculated band contour assuming an upper rotational constant of 0.0625 cm^{-1} and a lower rotational constant of 0.1245 cm^{-1} . This band is an $\Omega' = 4 - \Omega'' = 3$ (perpendicular) transition with a 'near Boltzmann' rotational temperature of $\approx 4\text{K}$ in the lower state.

CoAr^+ A'-X (14,0) Transition

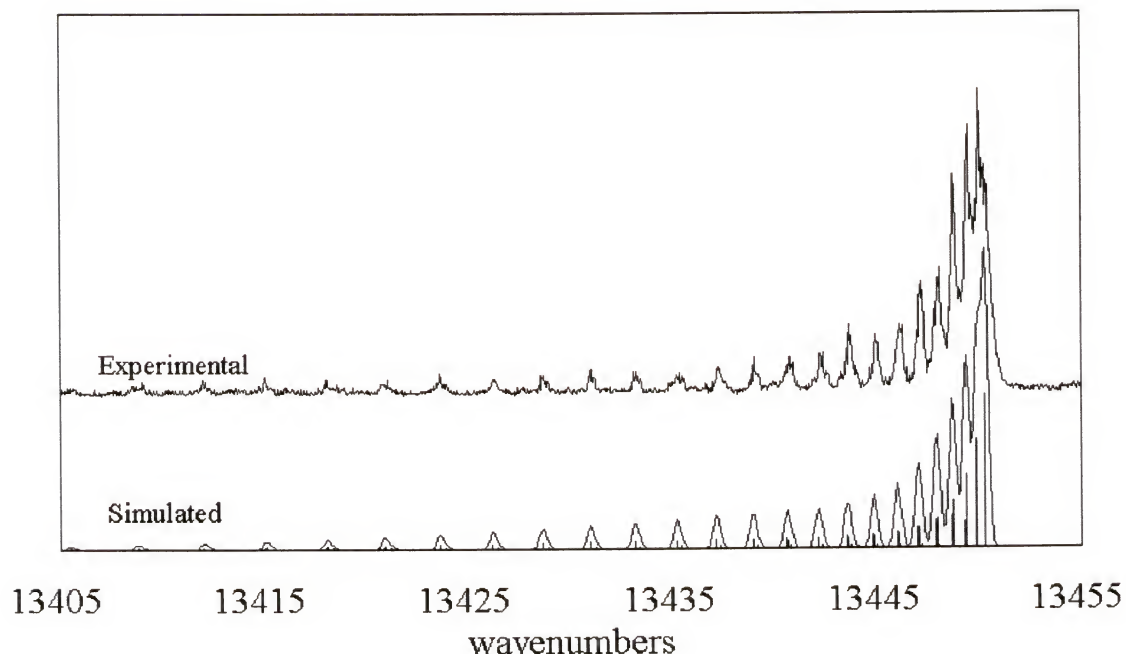


Figure 16. The CoAr^+ A'-X (14,0) Band.

The figure shows a closeup of the A'-X (14,0) band showing rotational structure. The upper trace is an experimental spectrum and the lower is a calculated band contour assuming an upper rotational constant of 0.0603 cm^{-1} and a lower rotational constant of 0.1245 cm^{-1} . This band like the previous is an $\Omega' = 4 - \Omega'' = 3$ (perpendicular) transition with a 'near Boltzmann' rotational temperature of $\approx 4\text{K}$ in the lower state. Fitting many or all of the rotational bands like this allows the determination of α_e for the CoAr^+ A' electronic state.

and are listed in **Table II**. All transitions seen in this figure originate from $v''=0$, i.e. no 'hot bands' are seen.

The upper states in the transitions in **Figure 14** have been arbitrarily lettered a, A', and B' in order of increasing electronic term energy, which, in this case, is in order of increasing transition frequency. The lettering of the higher-lying states in ref 8 of A, B, and C is retained as much as possible, however, the A state has been renamed as b since it belongs has been determined to be spin forbidden. The A'-X transition is indicative of an electronic transition in which a large geometry change of the molecule occurs upon excitation. This is evidenced in the spectrum by the long upper state vibrational progression and the red degraded rotational band structure of each vibronic transition. The previously observed transitions in this ion did not show such sharp rotational structure, presumably because of a shorter upper state unimolecular dissociation lifetime for the higher-lying states leading to homogeneous broadening of the transitions they involve. The B'-X transition shows a shorter progression and higher upper state vibrational frequency indicative of an upper state with a shorter equilibrium bond and greater binding energy than the A' state but still more weakly bound than the ground state. The a-X transition has just two observed bands with intensity peaking at the origin, implying an upper state of similar geometry to the ground state. Note that the intensity of the a-X bands is much greater than that which appears; the a-X bands in **Figure 14** have been reduced because these bands have been severely distorted due to detector saturation in this low-resolution scan.

Figure 15 shows a 'closeup' of the (13,0) band in the A'-X electronic transition.

The upper trace shows the experimental photodissociation spectrum and the lower trace is a contour simulation under the assumption that the CoAr⁺ molecule is a rigid-rotor symmetric-top. The simulation is generated via convolution of a instrument function (Gaussian, FWHM = 0.15 cm⁻¹, slightly broader than the laser linewidth) with the calculated line positions and intensities to obtain a parameterized rotational band contour. The excellent agreement between the experimental and simulated spectrum indicates the A'-X system is an $\Omega' = 4 - \Omega'' = 3$ (perpendicular) transition with a large decrease in rotational constant upon excitation. The rotational constants determined from the fit of this band are $B'' = 0.1245 \text{ cm}^{-1}$ for the ground state and $B' = 0.0625 \text{ cm}^{-1}$ for the upper state which yields a vibrationally averaged bond length of 2.385 Å and 3.366 Å for those states respectively.

Figure 16 shows another fit of the A'-X (14,0) band. Fits of nearly all of the bands in the A' state give a good idea of how the rotational constant changes with the vibrational quantum number v shown in Figure 17. This in turn gives an average bond length with v and can predict the r_e for the A' excited state, which is shown in Figure 18, and the vibration-rotation coupling constant. As the vibrational number increases, the average internuclear distance increases, due to the anharmonicity of the potential, and the rotational constant decreases. This decrease is given by:

$$B_v = B_e - \alpha_e(v + 1/2) \quad (4)$$

Table II. Known CoAr⁺ Transitions.

v'	a-X	A'-X	B'-X	A-X	B-X	C-X
0	12553.75	12399.36	13195.72			14544.7
1	12673.85	12499.83	13341.68			14714.3
2		12595.39	13482.22			14878.6
3		12687.03	13626.49			15034.7
4		12774.43	13763.84			15184.7
5		12858.32	13897.66			15328.2
6		12938.09	14023.49	14026.3	14076.8	15466.1
7		13013.81	14145.49	14149.0	14167.2	15598.6
8		13086.53	14252.00	14265.4	14254.4	15725.0
9		13155.03	14335.46	14375.7	14338.0	15845.1
10		13219.69	14398.45	14488.3	14418.7	15960.1
11		13280.70			14494.6	16069.5
12		13338.10			14567.6	16173.8
13		13392.08			14636.6	16272.0
14		13442.98			14701.9	16364.9
15		13490.19			14763.8	16453.0
16		13534.49			14822.5	16535.4
17		13575.32			14877.7	16614.1
18		13613.27			14930.1	16686.0
19		13648.21			14979.3	16754.9
20		13680.47			15025.6	16817.8
21		13710.08			15067.6	16875.9
22		13736.87			15106.7	16930.4
23		13761.06			15142.9	16979.8
24		13782.93			15176.9	17025.0
25		13802.48		15502.2	15207.7	17066.9
26		13819.73		15536.3	15236.1	17104.4
27		13835.06		15565.9	15261.3	17138.8
28		13848.70		15592.6	15284.9	17169.4
29		13860.45		15616.7	15305.3	17197.0
30		13870.56		15637.5	15323.3	17221.8
31		13879.33		15656.7	15340.2	17243.2
32		13886.81		15672.9	15354.9	17262.5
33		13893.31		15687.3	15368.2	17279.6
34		13898.62		15699.5	15378.9	17294.6
35		13902.81		15710.7	15388.3	17307.3
36		13906.58			15396.6	17318.3
37		13909.34			15403.6	17327.8
38					15409.3	17336.1
39					15414.3	17343.1
40					15418.5	17348.9
41					15421.8	17353.9
42						17358.0
43						17361.3
44						17363.9
45						17366.1
46						17367.6

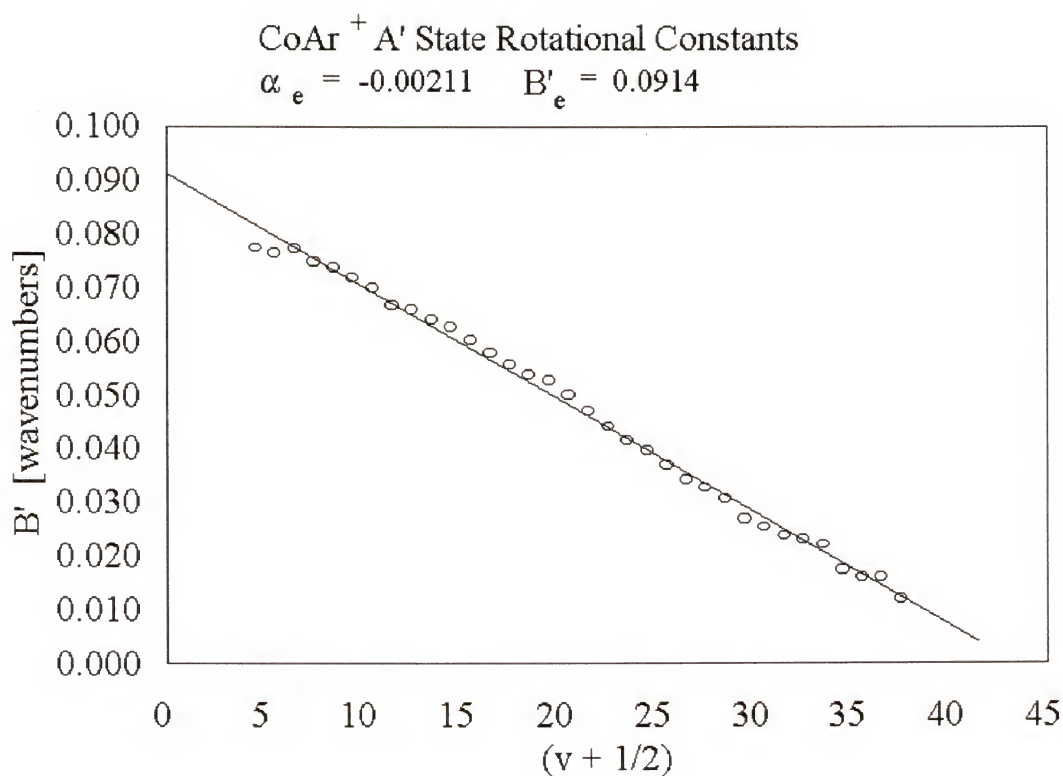


Figure 17. CoAr⁺ A' State Rotational Constant versus (v+1/2).

The figure shows a plot of the equilibrium rotational constants for vibrational levels in the A' electronic state. The constants are taken from the rotational fits for each of the observed vibrational levels. The B'_e versus (v+1/2) gives α_e which describes how fast the rotational constant or bond length changes with vibrational quantum number. For the A' electronic state $\alpha_e = -0.00211 \text{ cm}^{-1}$.

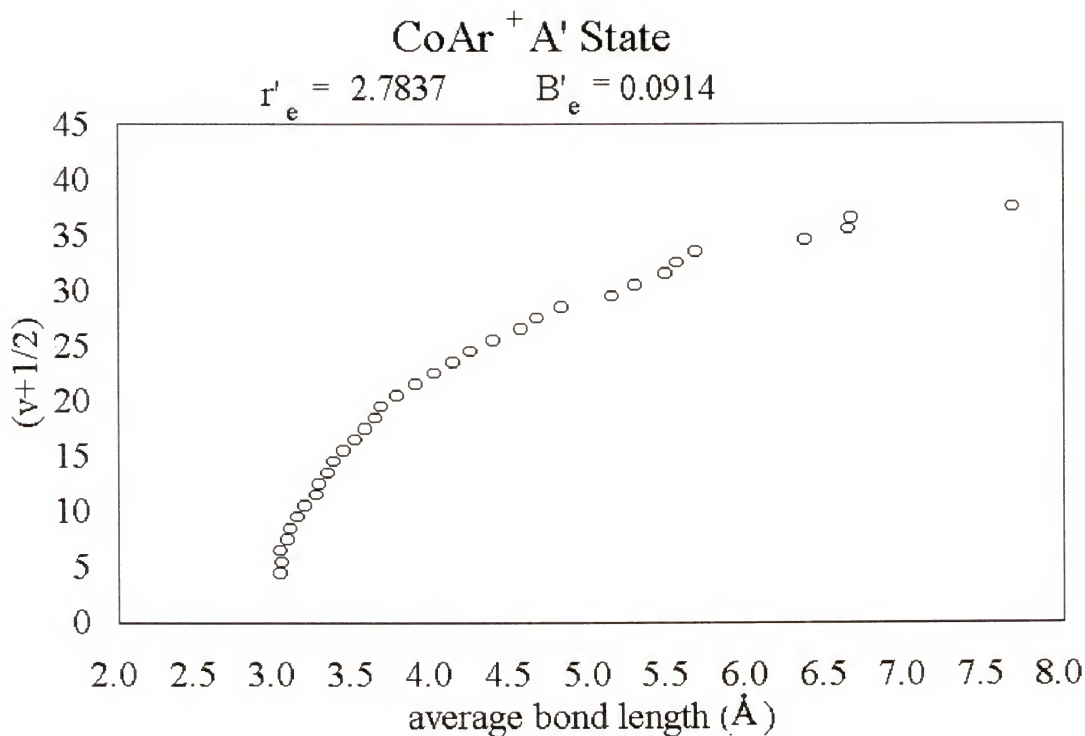


Figure 18. CoAr⁺ A' State r_e versus $(v+1/2)$.

The figure shows a plot of the equilibrium distances for vibrational levels in the A' electronic state. The r_e 's are taken from the rotational constants for rotational fits for each of the observed vibrational levels. The r_e versus $(v+1/2)$ gives an idea of what the potential looks like, except the inner and outer turning points are missing. A better picture would be r_e versus energy. A fit for r_e versus vibrational quantum number gives α_e which describes how fast the rotational constant or bond length changes with vibrational quantum number.

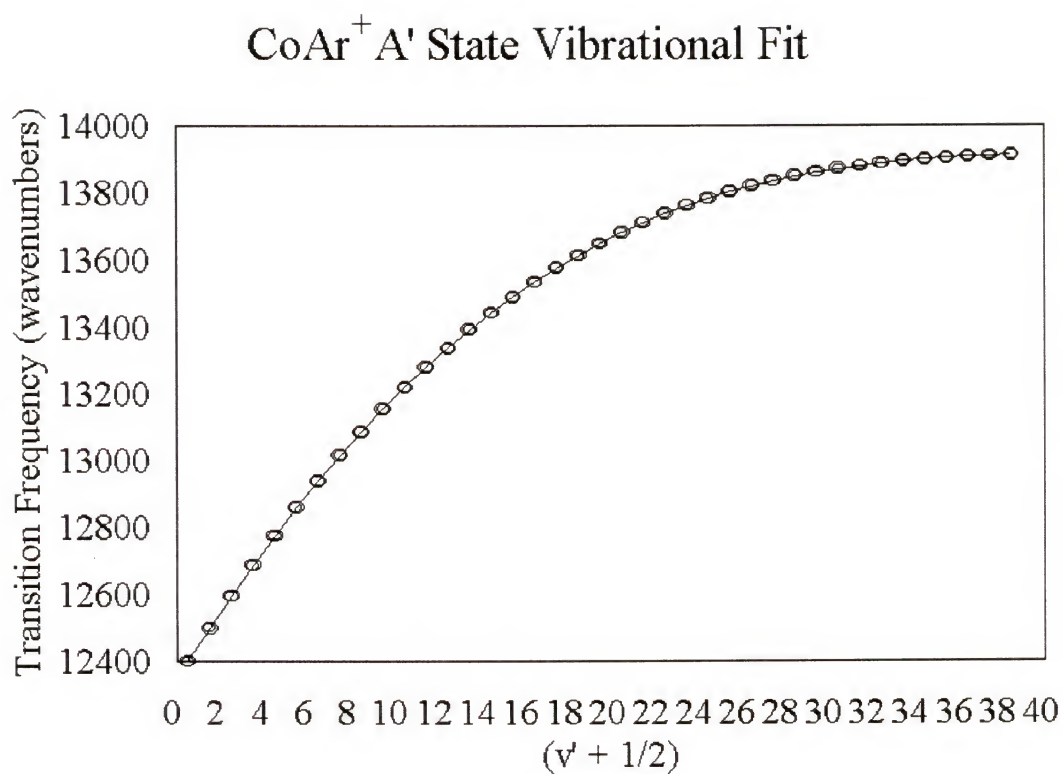


Figure 19. The CoAr⁺ A'-X Vibrational Fit.

The figure shows the Morse fit to the CoAr⁺ A' state. The line is the calculated value and the symbols are the experimental points. The error is too small to see on this scale. The residual errors (Observed - Calculated), shown in the next figure, are relatively small.

CoAr⁺ A' State Residuals

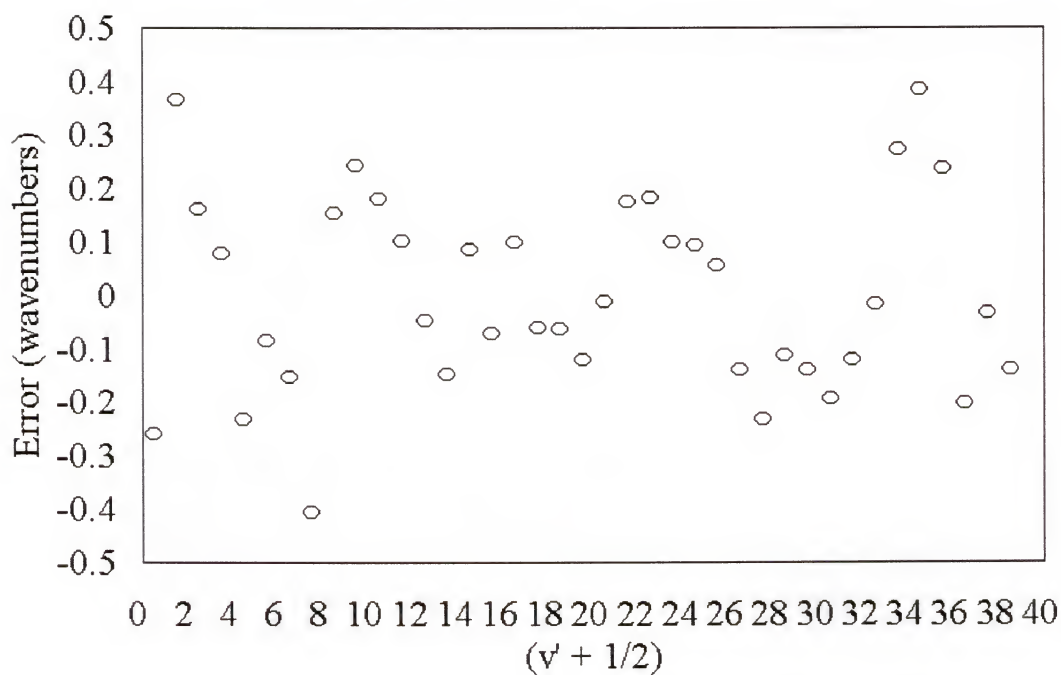


Figure 20. The CoAr⁺ A'-X Residuals to the Vibrational Fit.

The figure shows the residuals to a vibrational fit to the CoAr⁺ A' state. The symbols are the difference between the experimental points and the calculated line, $v_{v0} = T_{e0} + \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \dots$. The error is relatively small, less than 0.5 cm^{-1} .

The vibration-rotation coupling constant is found, from the slope, to be

$\alpha_e = -0.00211 \text{ cm}^{-1}$ and the equilibrium rotational constant $B_e' = 0.0914 \text{ cm}^{-1}$ which gives an equilibrium bond length of $2.784 \text{ \AA}$ for the A' state.

Figure 19 shows a Morse fit to the vibrational progression of the A' state which is embarrassingly good. Figure 20 helps show how poor the fit is. The residuals are all less than $\pm 0.5 \text{ cm}^{-1}$ and which corresponds to a fit with a correlation of ca. 1.0. These two rather simplistic figures are only given here to convey the accuracy of the techniques being used. Fits for other molecules in this dissertation are performed in a similar manner and have approximately the same error unless noted otherwise.

The stretching frequency of the A' state is found to be $\omega_e = 104 \text{ cm}^{-1}$ with an anharmonicity of $\omega_e x_e = 2.07 \text{ cm}^{-1}$. Many of the spectroscopic parameters for the A' and all known states of CoAr^+ are tabulated in Table III. The line positions of the various states listed in Table II have been displayed graphically in Figure 21 to give a clear picture of the relative positions of the states.

Figure 22 shows a closeup of the origin band of the a -X system. The fit of this band indicates that this system is a $\Delta\Omega = -1$ transition from the same $\Omega'' = 3$ ground state as in Figure 15. Here the rotational constants obtained from the fit are $B'' = 0.1245 \text{ cm}^{-1}$ for the ground state and $B' = 0.1172 \text{ cm}^{-1}$ for the upper state, indicating an upper state bond length of $2.458 \text{ \AA}$, only slightly longer than that of the ground state.

Figure 23 shows a resolved band in yet a third system, the B' -X (3,0). Since the ions in the beam are vibrationally and electronically cold, all the bands must (and do) show a consistent value of lower rotational constant. The B' state of CoAr^+ has an equilibrium

Table III. Properties, in wavenumbers, of the observed states of CoAr^+ .

State	T_{e0}^i	ω_e	$\omega_e x_e$	$\omega_e y_e$	D_e
X					4111 ⁱⁱ
a	12493	120.1			
A'	12353	104.0	2.07	0.004	1567
B'	12808	159.9	2.14		
A ⁱⁱⁱ	13081	165.4	3.20	0.017	2677
B ⁱⁱⁱ	13380	120.9	2.21	0.011	2053
C ⁱⁱⁱ	14458	175.8	3.28	0.016	2912

ⁱ T_{e0} is the electronic term energy relative to the zero point level of the X state

ⁱⁱ $D_0 \pm 5 \text{ cm}^{-1}$

ⁱⁱⁱ Reported previously in Reference 8.

bond length (2.746 Å in $v=3$) that is intermediate to that of the A' and a states. Note that the 'length' of the upper state vibrational progression to that of the B'-X transition is also intermediate of the A'-X and a-X transitions.

More information is yielded in the rotational contour than just the rotational constants. The simulation of the spectrum that we have generated is admittedly crude; a rigid symmetric top simulation; and thus the branch intensities are expected to be somewhat inaccurate, but the comparison with the observed spectrum yields an estimate of the rotational temperature of the ions in our beam: <4 K. However, the lower panel in Figure 12 has been generated with a rotational distribution not described by a single Boltzmann but a composite of 97% (3.8 K) ions and 3% (20 K) ions. This seems to adequately fit the high J 'tail' to the band shape. This 'tail' may be the result of the 'freezing in' of rotational energy as the collision energy drops during supersonic expansion.

CoAr⁺ Excited States

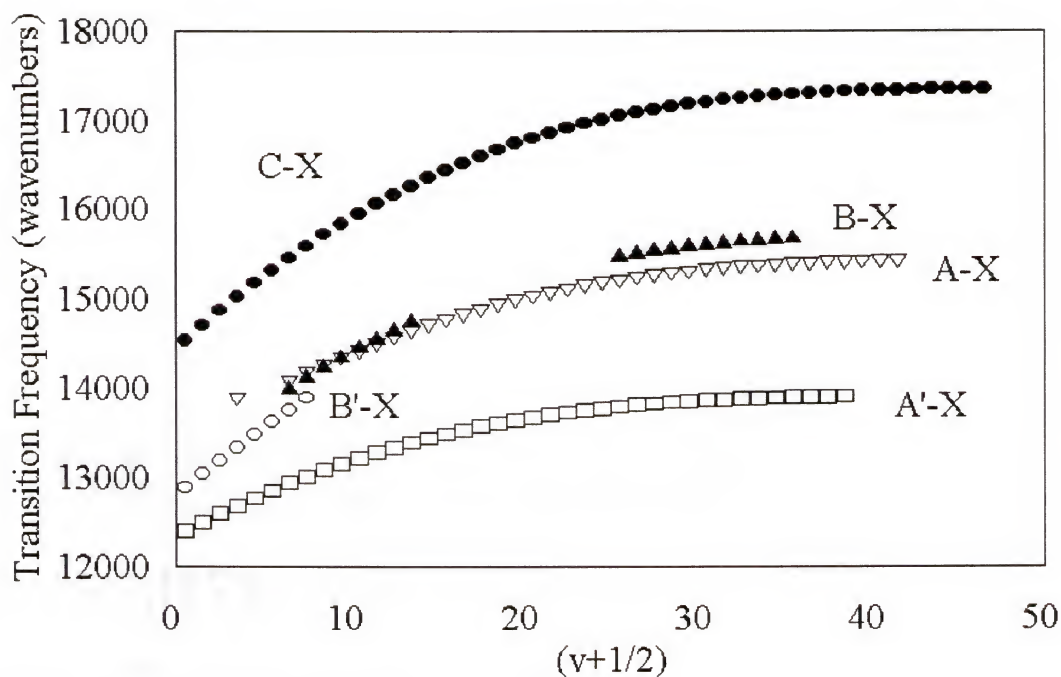


Figure 21. The Known CoAr⁺ States and Transitions.

The figure shows the various known transitions for the observed states in CoAr⁺. The states have been labeled according to their dissociation limits a, A', B', A, B and C. The absolute vibrational numbering of these states may change since isotopic analysis has not been possible. The best attempts have been made to the correct assignments in the absence of that data.

CoAr^+ a-X (0,0) Transition

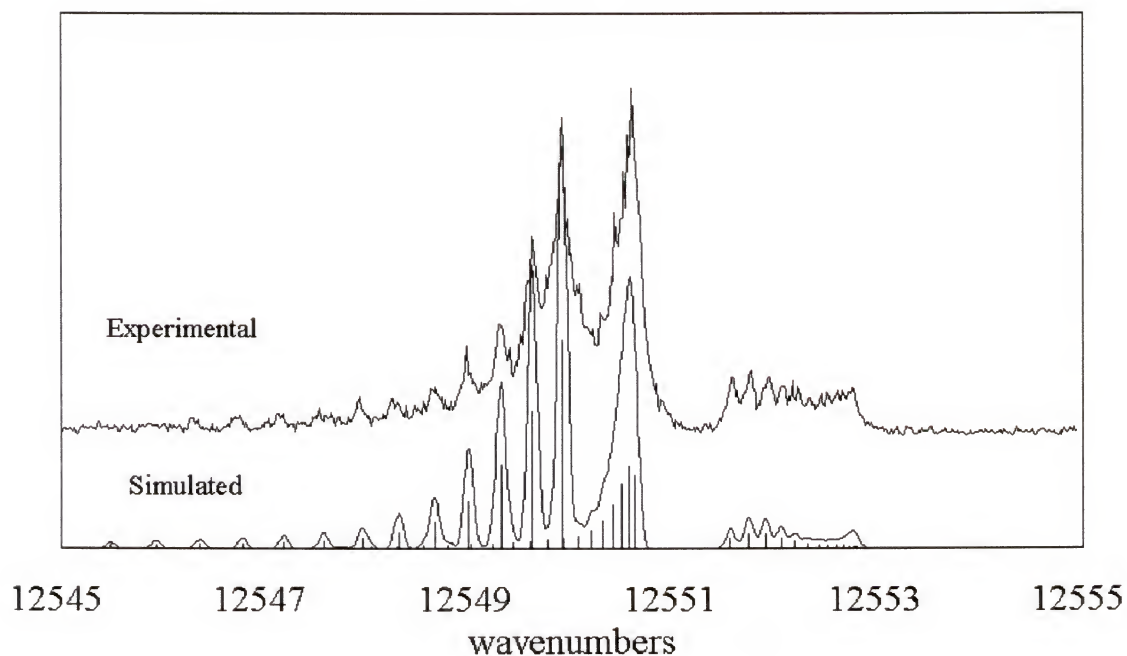


Figure 22. The CoAr^+ a-X (0,0) Band.

The figure shows a closeup of the spin forbidden a-X (0,0) origin band. This band is part of a $\Omega' = 2 \leftarrow \Omega'' = 3$ system with the same lower state as that in Figure 15 but with an upper state exhibiting a rotational constant of 0.1172 cm^{-1} . Again the upper trace is the experimental spectrum and the lower trace is calculated with the same rotational energy distribution as in Figure 15.

CoAr^+ B'-X (3,0) Transition

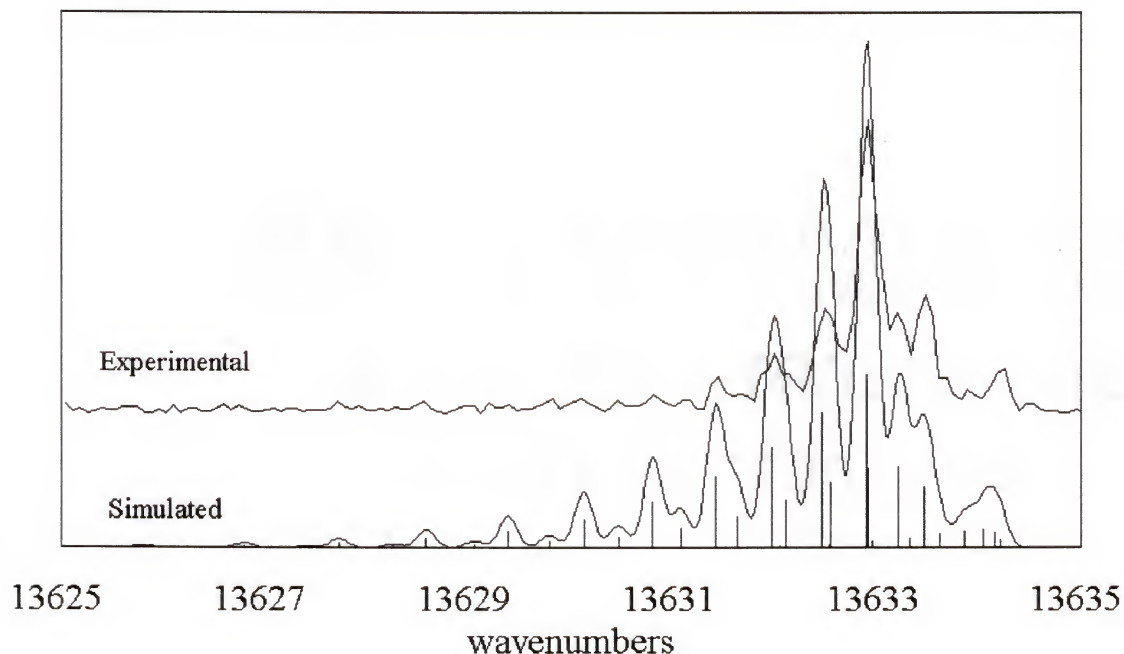


Figure 23. The CoAr^+ B'-X (3,0) Band.

The B'-X (3,0) band of CoAr^+ . This is another $\Omega' = 2 - \Omega'' = 3$ band with the same lower state as Figure 11 and Figure 12. Since all bands with reasonable intensity that can be rotationally resolved have the same lower-state rotational constant and Ω'' value, we conclude that these values correspond to the electronic ground state. The upper trace is the experimental spectrum and the lower is a contour simulation with a rotational constant of 0.0939 cm^{-1} .

Nonetheless, the bulk of these charge-(induced-dipole) bound ions appear to be slightly rotationally colder than metal dimer ions (Ni_2^+) formed in the same source¹⁰.

LeRoy-Bernstein analysis¹¹ of the vibrational structure of the upper states in an electronic transition yields the diabatic dissociation limit of that state. This treatment shows that a diatomic molecule will exhibit vibrational structure near dissociation that is determined by the longest-range attractive force between the separated atoms. For CoAr^+ , this force is charge-(induced-dipole) and scales like $1/r^4$. In this case, a plot of $(\{G(v'+1) - G'(v'-1)\}/2)^{4/3}$ versus transition frequency is linear near dissociation and may be used to confidently extrapolate experimental band origins to the convergence at D_0 . This procedure has been applied⁸ to two assigned dissociation limits of the CoAr^+ molecule previously, and similar analysis yields a value of 13920 cm^{-1} for the A' state observed in this study and is shown graphically in **Figure 24**. This confirms the diabatic dissociation limit of the A' state as $\text{CoAr}^+ \rightarrow \text{Co}^+ d^7s (^3F_4) + \text{Ar} (^1S)$. **Table IV** shows the observed dissociation limits of CoAr^+ . Three upper state dissociation limits are directly observed. The ground state limit is calculated from the observed limits and the known energy levels of the Co^+ ion¹².

Table IV. The Dissociation Limitsⁱ, D_0 , of CoAr^+ .

$\text{Co}^+ d^8 (^3F_3) + \text{Ar} (^1S)$	$4111 \pm 5 \text{ cm}^{-1}$	Ground State Bond Strength
$\text{Co}^+ d^7s (^3F_4) + \text{Ar} (^1S)$	13920 cm^{-1}	A' State convergence
$\text{Co}^+ d^7s (^3F_2) + \text{Ar} (^1S)$	15433 cm^{-1}	B State convergence
$\text{Co}^+ d^8 (^3P_2) + \text{Ar} (^1S)$	17370 cm^{-1}	C State convergence

ⁱ All dissociation limits are referenced to $\text{CoAr}^+ X ^3\Delta_3 (v=0)$.

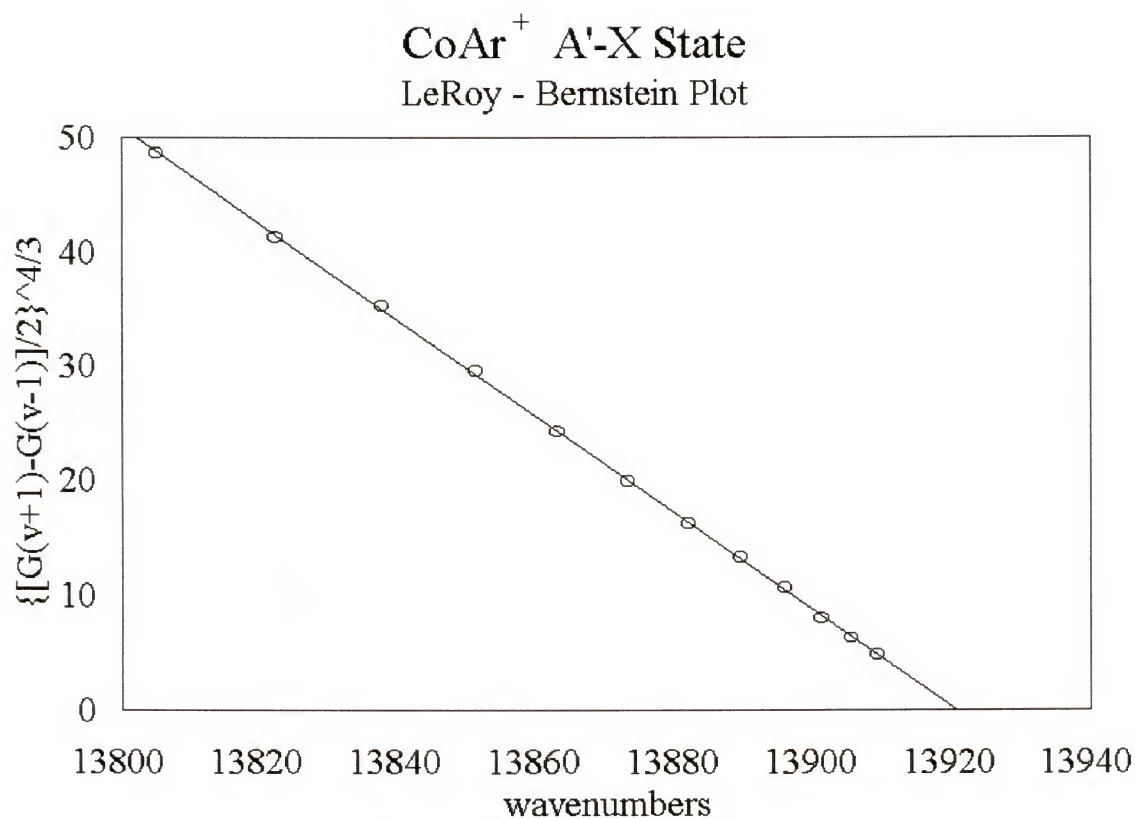


Figure 24. CoAr⁺ A' State LeRoy-Bernstein Fit.

The figure shows a dissociation limit from the LeRoy-Bernstein fit of the A' state. The plot is of the derivative of the $\Delta G'(v)^{4/3} = [\{G'(v+1)-G'(v-1)\}/2]^{4/3}$ versus transition frequency for the observed energy levels.

Ground State of CoAr⁺

The ground state predicted by *ab initio* theory⁹ for CoAr⁺ is $^3\Delta_3$ with a binding energy of $D_0 = 0.402$ eV (3240 cm^{-1}) when corrected for zero point and spin-orbit effects. As the binding of this molecule is electrostatic, the ground state should be formed from the electronic configuration of the open shell metal ion that minimizes bond-axis electron density and thus minimizes repulsion with the polarizable argon. Of the low-lying configurations of the Co⁺ ion, the d^8 (ground state) is expected to be more strongly bound to Ar than the excited d^7s configuration based on its smaller effective ionic radius. This idea has been experimentally verified for excited states of transition-metal rare-gas ion complexes¹³. Within the d^8 atomic configuration, the d-holes in the Co⁺ ion should align upon molecule formation to minimize repulsion and maintain triplet spin coupling. Using this molecular-orbital overlap argument, the possible candidates for the ground state of the molecule would be either a $^3\Pi\ 3d\sigma^1 3d\pi^3 3d\delta^4$ (a $\sigma\pi$ -hole) state or a $^3\Delta\ 3d\sigma^1 3d\pi^4 3d\delta^3$ ($\sigma\delta$ -hole) state. Bauschlicher⁹ has calculated the $^3\Delta$ state to be $\approx 500\text{ cm}^{-1}$ lower than the $^3\Pi$ at the SOCI+Q level. The spin orbit splitting in the bare Co⁺ is large and inverted so the ground state of the ion is the highest Ω component of the multiplet, i.e. either $^3\Pi_2$ or $^3\Delta_3$. Our rotational analysis indicate $\Omega'' = 3$ and thus assigns the ground state of CoAr⁺ as $^3\Delta_3$.

Experimentally, the symmetry of the ground state predicted by theory may be correct, but the binding energy predicted by theory is found to be $\approx 20\%$ too low. This error is systematic and has been observed for other $M^+\cdot\text{RG}$ species for which this comparison can be made⁹. Nonetheless, the bond length calculated by Bauschlicher

compares very favorably with the experimental result. It is found that the $^3\Delta$ has an equilibrium internuclear distance of $r_e = 2.4326\text{\AA}$ at the MCPF level and $r_e = 2.4395\text{\AA}$ at the SOCI+Q. Experiment yields a vibrationally-averaged bond length in the zero point level of the ground state which is only slightly shorter: $r_0 = 2.385 \pm 0.005\text{\AA}$.

The ground state bond length of CoAr^+ predicted empirically in reference 8 is ridiculously short. The electrostatic model used in that paper related experimental dissociation energies and vibrational frequencies for excited states, and worked well, but does not predict valid r_e values. Obviously, *ab initio* theory provides good bond lengths for these simple inductively bound systems, shown to be just 2% greater of the experimental value for the CoAr^+ ground state.

Experimental methods are being devised in our lab to test the theoretical predictions of ground state vibrational frequencies of this and other transition metal ion clusters. The excited state information (frequencies, anharmonicities, in some cases RKR potential) that we obtain from excitation spectroscopy is not yet calculable by *ab initio* methods. It is hoped that complete experimental detail regarding a charge-(induced-dipole) bound open d-shell system will provide a benchmark for empirical and *ab initio* theory.

Nickel Argon Cation

Low-lying metastable states of molecules are of interest because of the important role they play in chemistry. Because these states have 'wrong' spin to radiate, they may pool energy, and may have subtle and selective relaxation mechanisms. In fact, these

excited states may possess rather different properties than the ground state or other states of the ground state multiplicity. Transition-metal containing molecules have a large number of accessible excited electronic states and the role of these excited electronic states in the chemistry of transition metal atomic ions is well documented¹⁴. *Ab initio* theory has a hard time with transition metals because of this complexity, but simple electrostatic complexes of a metal ion with a rare gas should be tractable. This type of molecular ion is not trivial and has a variety of interesting properties. The atomic ion in the complex is 'lumpy' by virtue of its open d-shell and may bind differently depending on the orientation of these orbitals. The molecule is expected to have a large spin-orbit coupling between Born-Oppenheimer surfaces. These MAr^+ ions also have many low-lying electronic states arising from several distinct electronic configurations, in likeness to more complicated inorganic complexes.

Although metastable excited states are difficult to access through optical spectroscopy from the electronic ground state, this is exactly what has been performed in the characterization of the first quartet states of NiAr^+ in the following study.

Figure 25 shows the photodissociation of NiAr^+ into Ni^+ induced by the dissociation laser as it is tuned in frequency in the near IR. The vertical axis in all the spectra presented here is the relative Ni^+ fragment photocurrent resulting from the excitation of mass-selected NiAr^+ which is the only fragment ion mass observed. It is easy to generate space-charge limited quantities of this parent ion, or about 10^9 ions/ $\text{cm}^3 \cdot \text{pulse}$, but the fragmentation signal obtained in this experiment is much weaker than observed for similar species such as CoAr^+ ion⁸ and VAr^+ ion¹³. The magnitude of dissociation is so

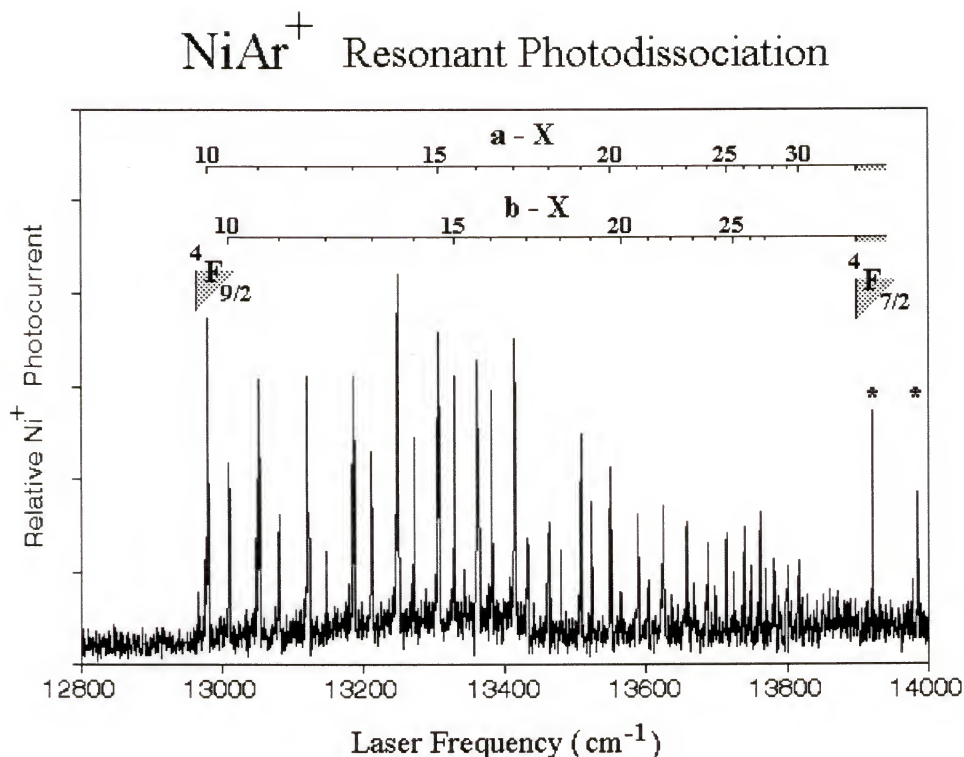


Figure 25. The NiAr^+ a and b States.

The figure shows a portion of the resonant photodissociation spectrum of the NiAr^+ ion in the region of 12800 - 14000 cm^{-1} . Two progressions of vibronic bands, labeled a-X and b-X converge to the $\text{Ni}^+ \text{}^4\text{F}_{7/2} + \text{Ar } ^1\text{S}$ dissociation limit, are labeled as to the absolute upper vibrational quantum number of the transition as determined by isotope shift analysis. The threshold for $\text{Ni}^+ \text{}^4\text{F}_{9/2} + \text{Ar } ^1\text{S}$ fragments is shown as a grey triangle and marks the red cutoff of both the a-X and b-X progressions. The beginning of the c-X progression is marked with an asterisk. The break in intensity at about 13400 cm^{-1} is due to a change in dissociation laser power and is not an intrinsic feature of the spectral intensities.

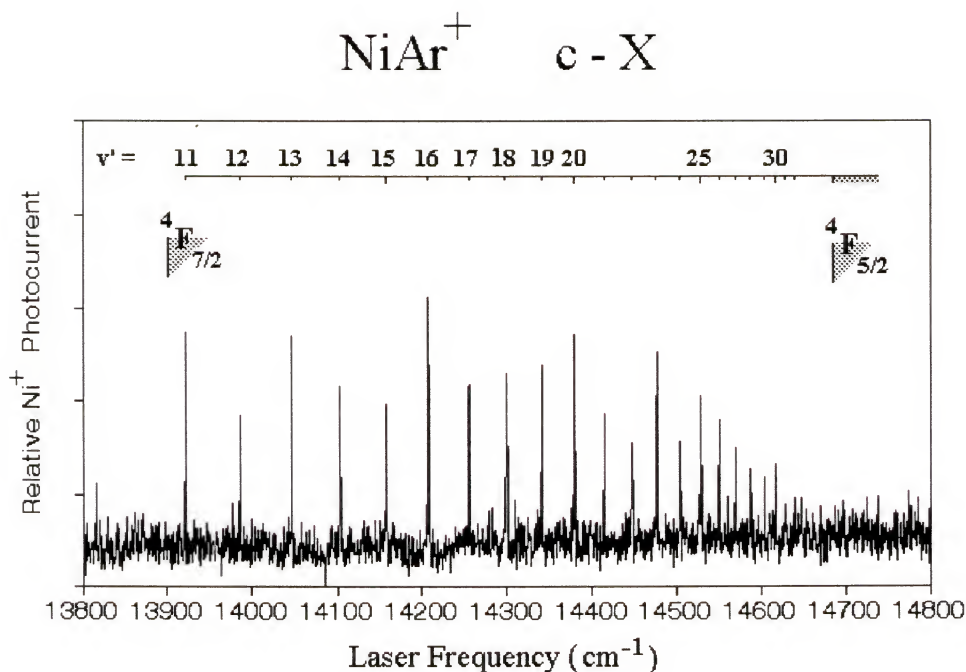


Figure 26. The NiAr^+ c State.

The figure shows a continuation of the dissociation action spectrum in **Figure 25** and the c-X upper state vibrational progression converging to the $\text{Ni}^+ \text{}^4\text{F}_{5/2} + \text{Ar } ^1\text{S}$ limit. Note the red cutoff of the c-X progression is at the $\text{Ni}^+ \text{}^4\text{F}_{7/2}$ limit in analogy to the breaks in the a-X and b-X progressions at the $\text{}^4\text{F}_{9/2}$ limit. Again the upper state vibrational quantum number of these cold band transitions, obtained from isotope shifts, as will be shown for the a-X progression.

small, only 1 part in 10^7 at 20 mJ/cm^2 •pulse dissociation laser fluence, collision-induced dissociation of the parent in the 2.5 m long flight tube (pressure 2×10^{-8} Torr, mostly He residual gas) contributes to the baseline of the data in **Figure 25** and **Figure 26**. Previous spectra obtained in this apparatus were free of this interference. The dissociation fluence employed here is relatively high for this apparatus, and as a result, a detectable contribution to the fragmentation from non-resonant multi-photon processes is also observed. This phenomenon adds the easily distinguished 'dye power curve' to the baseline of the action spectra. With all this advised, it is clear that a resonant dissociation spectrum is evident in **Figure 25**, well below the energy of the first excited doublet states of the ion and in the region of the first quartet limits. Since the spectra for these states is particularly difficult to observe, no apologies for the marginal signal-to-noise ratio will be made.

The weak resonant dissociation features in the spectrum in **Figure 25** are the result of a spin-forbidden one-photon absorption following a spin-orbit induced predissociation. Two electronic transitions which exhibit long upper state vibrational progressions are seen in **Figure 25**. The progression clearly samples the upper bound regions of the upper state potential since the bands converge as they disappear to higher frequency. Both progressions start abruptly at about $12\,970 \text{ cm}^{-1}$ which might, at first glance, be interpreted as an electronic origin. In other words, one might be tempted to label the reddest band of each progression as the (0,0) of the transition. However, the break in intensity is due to a change in the dissociation yield of the upper state and not to a change in absorption strength. Simultaneous acquisition of the spectra of two isotopic variants of

Table V. NiAr⁺ a-X, b-X and c-X Transition Frequencies and Absolute ν' .

ν'	(a-X)	(b-X)	(c-X)
10	12977.23	13007.82	
11	13050.09	13078.47	13919.03
12	13118.55	13145.82	13983.65
13	13184.22	13209.55	14044.18
14	13246.37	13270.19	14101.68
15	13304.81	13326.69	14155.52
16	13359.35	13380.25	14206.03
17	13411.48	13430.28	14253.40
18	13459.34	13477.37	14297.75
19	13504.60	13521.48	14339.07
20	13546.89	13562.24	14377.37
21	13585.86	13599.81	14412.64
22	13621.85	13634.73	14445.19
23	13654.66	13666.45	14474.73
24	13684.72	13695.82	14501.54
25	13712.42	13722.11	14526.38
26	13736.66	13745.62	14548.40
27	13759.42	13766.92	14567.81
28	13779.20	13786.45	14585.34
29	13797.01	13802.04	14600.89
30	13812.59	13817.87	14614.35
31	13826.70		14626.87
32	13838.81		14636.89
33	13848.95		14644.92
34	13858.36		14651.71
35			14658.25

the molecule, i.e. $^{58}\text{Ni}^{40}\text{Ar}^+$ and $^{60}\text{Ni}^{40}\text{Ar}^+$, allows the determination of the absolute vibrational quanta of the transitions (see below). Note that all the transitions observed are cold; that is, have the zero point level of the ground state as their lower level. The first observed transition in each progression starting at about 12 970 cm^{-1} is actually $\nu'=10$.

Figure 26 features the spectrum of a third vibrational progression of which only the reddest two members can be seen in Figure 25. For convenience, we have labeled the three upper electronic states observed in Figure 25 and Figure 26 as a, b, and c in order of increasing term energy (the ground electronic state is labeled X). The a and b states share the same diabatic dissociation limit and have an apparent difference in vibrational frequency and rotational band contourⁱ.

Figure 27 shows an accurate determination of the diabatic dissociation limits of the a, b, and c states via an extrapolation of a power of the vibrational first differences as described by LeRoy and Bernstein¹¹. This treatment shows that a diatomic molecule will exhibit vibrational structure near dissociation that is determined by the longest-range attractive force between the separated atoms. For NiAr⁺, this force is charge-(induced-dipole) and scales like $1/r^4$. In this case, a plot of $\Delta G'(v')^{4/3} = (\{G'(v'+1) - G'(v'-1)\} / 2)^{4/3}$ versus transition frequency is linear near dissociation and may be used to confidently extrapolate experimental band origins to the convergence at D_0 . This procedure has been applied successfully to MAr⁺ molecules previously, and comparable analysis is employed in this study. The a and b state dissociation limit are found to be 13 903 cm⁻¹ above the zero point of the ground state. The c-X limit is found at 14 688 cm⁻¹. These data are sufficient to assign the lower dissociation limit as corresponding to Ni⁺ ⁴F_{7/2} + Ar ¹S fragments and the upper one to Ni⁺ ⁴F_{5/2} + Ar ¹S. Subtraction of the promotion energy¹²

ⁱ The details of the rotational structure are not easily seen at the resolution of Figure 25 but the bands a-X transition show two prominent heads (Q,R) and the b-X only one. Full rotational analysis must wait for superior quality spectra.

of the d^8s (^4F_J) excited Ni^+ from that of its d^9 ($^2D_{5/2}$) ground state yields a ground state adiabatic bond energy, $D_0 = 4572 \pm 5 \text{ cm}^{-1}$.

Once the ground state binding energy is known, the energies of all the dissociation limits of the ion may be calculated from atomic terms. In particular, the $Ni^+ ^4F_{9/2} + Ar ^1S$ limit is predicted to be at $12\,966 \text{ cm}^{-1}$. The red cutoff of each of the a-X and b-X progressions correspond to this dissociation limit. Similarly, the break in the c-X progression at $v'=11$ corresponds to the $Ni^+ ^4F_{7/2} + Ar ^1S$ limit. These limits are marked by Ni^+ electronic state in Figure 25 and Figure 26.

The mechanism for dissociation is the coupling of the upper state to the manifold of levels correlating to the Ni^+ atomic limit of the same configuration but next lower in energy (next higher in J since all the multiplets are inverted). Note that multi-photon processes cannot be contributing significantly to the resonant fragmentation signal or the intensity break at the one-photon energy threshold would not be observed.

For a transition to be detected, the lifetime of at least a fraction of the optically prepared excited states must be shorter than the flight time between the laser excitation region and secondary mass analysis in our machine, or less than about $2 \mu s$ for this mass ion. Therefore, the excited quartet states with $v' > 10$ have a unimolecular dissociation lifetime of tens of microseconds at most. The lower limit to the lifetime of these levels is crudely given by the resolution of the spectrum; This implies an upper state lifetime greater than $1 ps$. Note that the excited state vibrational levels with $v' < 10$ are not detected at all which may be the result of very long lifetimes.

$^{58}\text{NiAr}^+$ LeRoy Bernstein

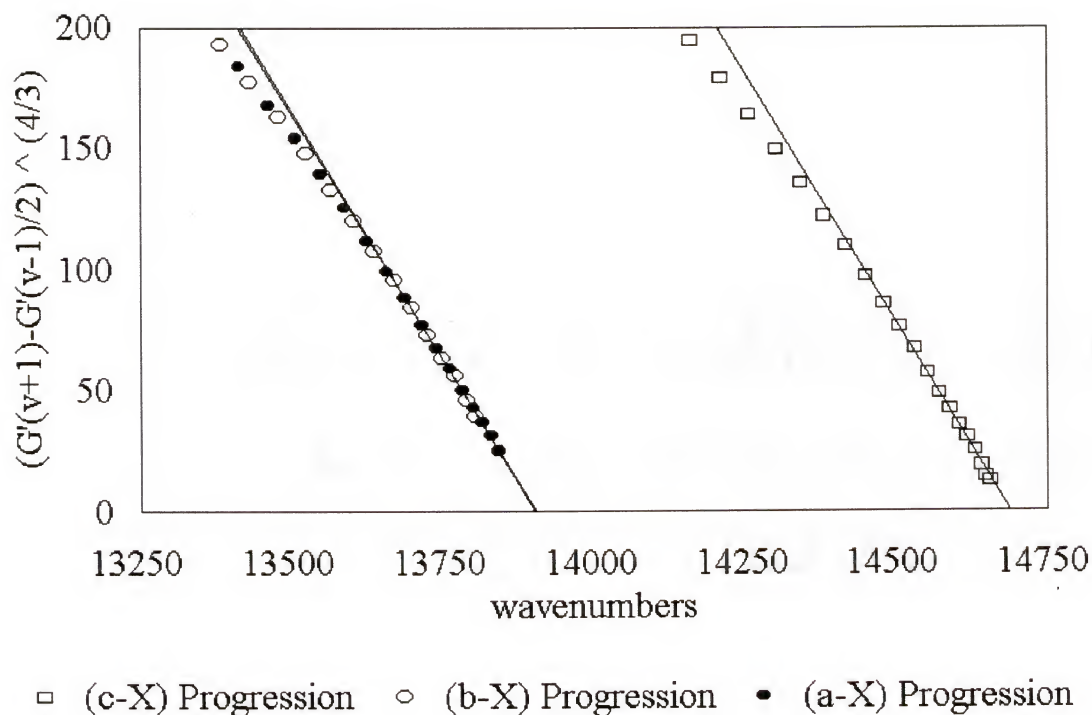


Figure 27. The NiAr^+ LeRoy-Bernstein Fits.

The figure shows LeRoy-Bernstein analysis of the convergence of vibrational levels to the dissociation limits of the quartet states of NiAr^+ . A $1/r^4$, charge-(induced-dipole), limiting form of the potential is assumed for this dissociation so a plot of $\Delta G'(v')^{4/3}$ versus transition frequency should be linear near the top of each potential. The a-X and b-X progressions converge to the $\text{Ni}^+ \text{}^4\text{F}_{7/2}$ limit at $13\,903\text{ cm}^{-1}$ and the c-X converges to the $\text{}^4\text{F}_{5/2}$ limit at $14\,688\text{ cm}^{-1}$.

Table VI. Properties, in wavenumbers, of the observed states of $^{58}\text{Ni}^{40}\text{Ar}^+$.

State	T_{e0}^i	ω_e	$\omega_e x_e$	$\omega_e y_e$	D_e
X	-113 ± 25	$225 \pm 50^{\text{iii}}$	-	-	$4685 \pm 25^{\text{ii}}$
a	11977	118	2.23	0.011	1926
b	12031	115	2.18	0.011	1872
c	12902	113	2.27	0.013	1786

ⁱ T_{e0} is the electronic term energy relative to the zero point level of the X state

ⁱⁱ $D_0 = 4572 \pm 5 \text{ cm}^{-1}$

ⁱⁱⁱ From the isotope shift of the $\text{Ni}^+(^2F_{7/2}) + \text{Ar } ^1S$ limit. see ref 12.

Conventional vibrational analysis³ of the vibronic band origins is performed on the bands listed in **Table V** to extract the spectroscopic constants of the excited states. As the progressions are very anharmonic, only the lowest 15 band origins are used in the determination of the electronic and vibrational constants in the standard formula:

$$v(v',0) = T_{e0} + \omega'_e(v'+1/2) - \omega_e x'_e(v'+1/2)^2 + \omega_e y'_e(v'+1/2)^3 \quad (5)$$

Note that the constant T_{e0} is the electronic term energy of the upper state relative to the zero point of the ground state potential and not relative to the ground state minimum. These constants are listed in **Table VI** for the major isotopic variant of the molecule in natural abundance, $^{58}\text{Ni}^{40}\text{Ar}^+$.

An important consideration in the interpretation of these spectra has been the assignment of the absolute upper state vibrational numbering through isotope analysis. **Figure 28** shows the predicted shift in the frequency of a transition in the $^{60}\text{Ni}^{40}\text{Ar}^+$ molecule relative to that of $^{58}\text{Ni}^{40}\text{Ar}^+$ for different choices of the vibrational quantum number assignment for the a-X progression. The heavy curve in the figure is the

prediction for the assignment of the vibrational quantum numbers as shown in Figure 25 and the light curves are the predictions for numberings shifted from 5 quanta lower to 5 quanta higher, i.e., assigning the first observed transition as the (5,0) through (15,0). The symbols indicate the observed isotope shifts which are consistent with only the chosen numbering.

The adiabatic bond strength of NiAr^+ has been measured before¹⁵ at 0.55 eV by the analysis of the threshold for production of $\text{Ni}^+ \text{ } ^2\text{F}_j + \text{ } ^1\text{S Ar}$ photoproducts from cold parent ions. This value is refined by the present results to give $D_0 = 4572 \pm 5 \text{ cm}^{-1}$. The error in the previous measurement was probably due to sloppy laser frequency calibration. The ground state binding energy predicted by *ab initio* theory⁹, $D_0 = 3270 \text{ cm}^{-1}$ is too small by nearly 30%.

Theory also predicts the properties of the lowest excited quartet state which arises from the $\text{Ni}^+ \text{ d}^8\text{s}$ configuration as opposed to the d^9 metal atom configuration of the ground state. Here, Bauschlicher *et al.*⁹ predicts the binding energy of a $^4\Delta$ state arising from this configuration of $D_0 = 1710 \text{ cm}^{-1}$ and $\omega_e = 109 \text{ cm}^{-1}$. If these values are compared with the average of the properties of the a, b, and c states of 1861 and 114 cm^{-1} , an error of only -8% and -4% is obtained. Of course, it is not yet known if the states seen in this study are in fact spin-orbit components of the $^4\Delta$ state; full rotational analysis will reveal this as well as the bond lengths of the ground and upper levels. Although the spectra observed here are weak, rotational analysis may be possible as was recently performed for red transitions in CoAr^+ ion¹⁶ and the spin forbidden transitions in ZrAr^+ .

NiAr^+ (a-X) Isotope Shift

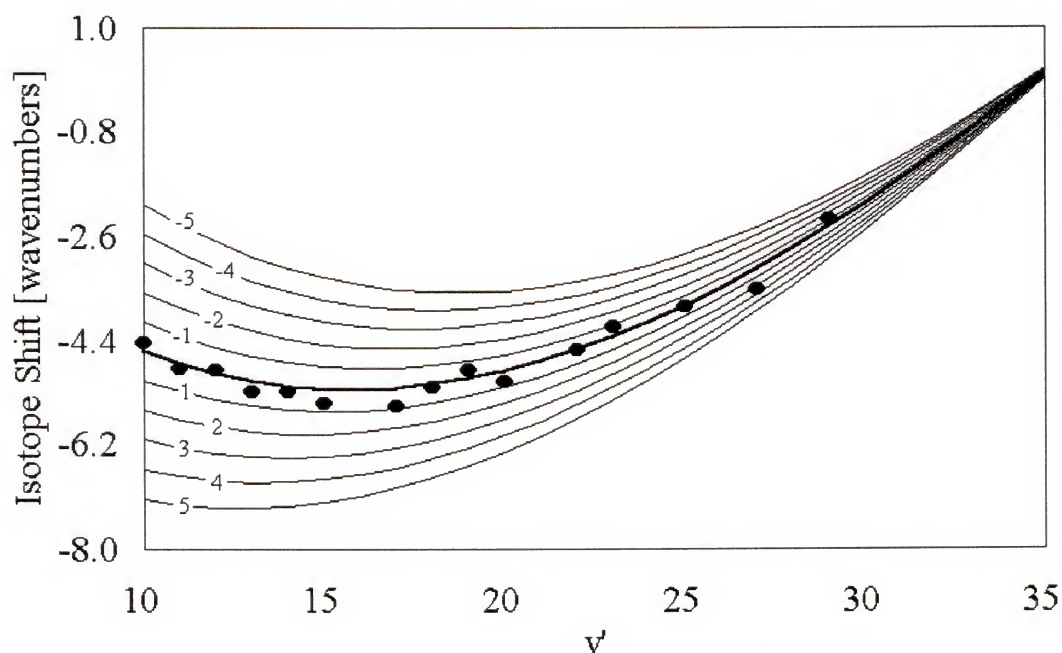


Figure 28. NiAr^+ a State Isotope Shift.

The figure shows the predicted (curves) and observed (symbols) shifts in the frequency of transitions in the $^{60}\text{Ni}^{40}\text{Ar}^+$ molecule relative to that of $^{58}\text{Ni}^{40}\text{Ar}^+$ for different choices of the vibrational quantum number assignment for the a-X progression. The heavy curve in the figure is the isotope shift predicted for the assignment of the vibrational quantum numbers as shown in Figure 25 and the constants of Table VI. The light curves are the predictions for numberings shifted lower or higher by ± 5 quanta, i.e., isotope shifts are calculated by assignment of the first observed transition in the a-X system as the (5,0) through (15,0). The symbols indicate the observed isotope shifts and are consistent with only the chosen numbering with the reddest band assigned as a-X (10,0).

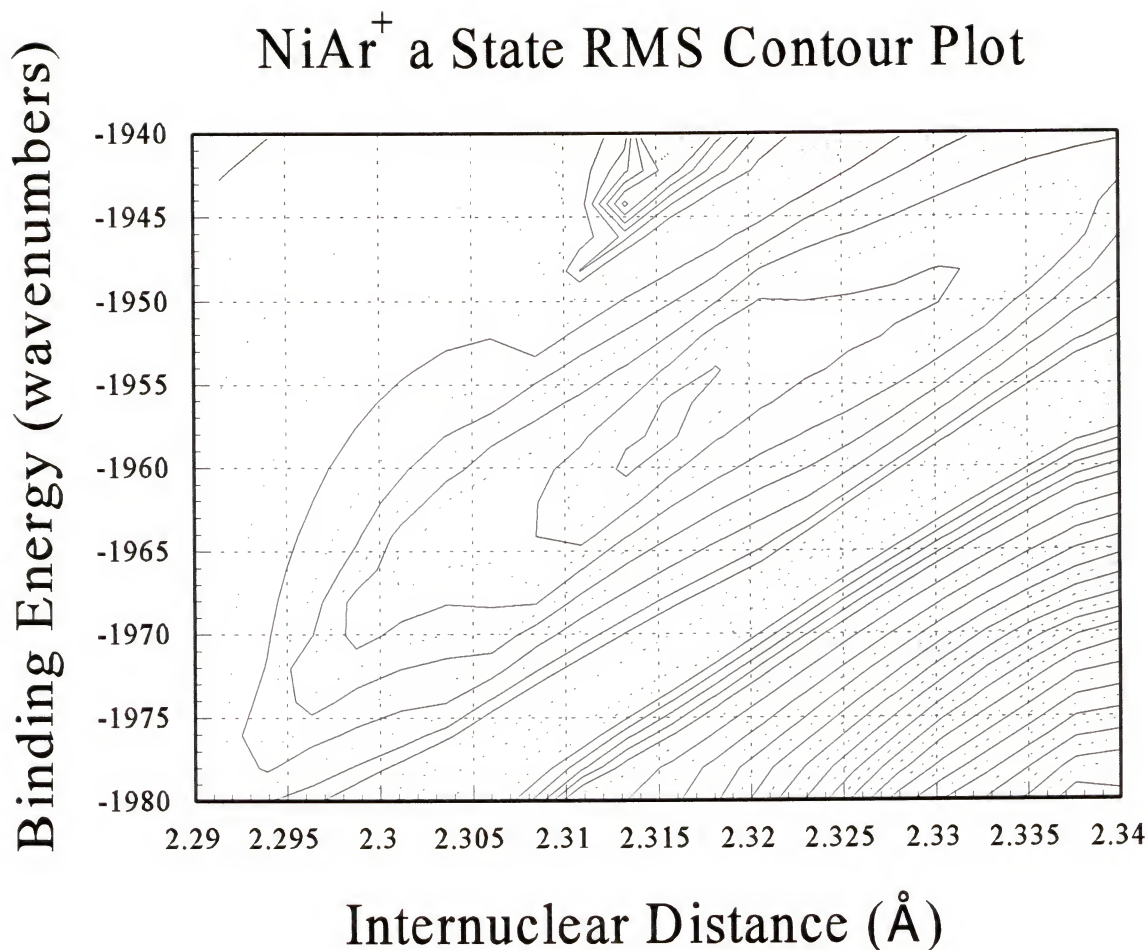


Figure 29. NiAr^+ RMS Plot for WKB Fit to Born-Meyer Potential.

The figure shows a root-mean-square plot for the observed vibrational levels versus the WKB predicted levels of the NiAr^+ spin forbidden a state. The two adjustable parameters in the Born-Meyer potential used in the WKB calculation are the dissociation energy and the vibrational frequency. The internuclear distance is directly related to these values and is plotted here versus the dissociation energy. The contours correspond to 0.5 cm^{-1} steps in dissociation energy. The agreement with the observed dissociation energy and vibrational frequency is quite good. WKB fit predicts $\omega_e=119 \text{ cm}^{-1}$, $D_e=1957 \text{ cm}^{-1}$ and $r_e=2.315 \text{ Å}$, while observed values for this state are $\omega_e=118$, $D_e=1926$ and r_e is as yet unknown.

WKB approximation¹⁷ has been used with a Born-Mayer potential to fit the observed vibrational energy levels of the NiAr^+ a state. The fit gives root-mean-square plot for the observed vibrational levels versus the WKB predicted levels of the NiAr^+ spin forbidden a state. The two adjustable parameters in the Born-Meyer potential used in the WKB calculation are the dissociation energy and the vibrational frequency. The internuclear distance is directly related to these values and is plotted here versus the dissociation energy. The RMS contours correspond to 0.5 cm^{-1} steps in dissociation energy. The agreement with the observed dissociation energy and vibrational frequency is quite good. WKB fit predicts $\omega_e=119 \text{ cm}^{-1}$, $D_e=1957 \text{ cm}^{-1}$ and $r_e=2.315 \text{ \AA}$, while observed values for this state are $\omega_e=118 \text{ cm}^{-1}$, $D_e = 1926 \text{ cm}^{-1}$. The poor resolution of this spectrum does not allow full rotational analysis, but an attempt to fit the rotational contour may provide the approximate r_e with a little work, and only slightly better data.

Zirconium Argon Cation

The photodissociation spectra of isolated, mass-selected ZrAr^+ have been observed previously¹⁸. What is reported here, however, extends the previous work by including rotationally-resolved spectra and dissociation limits of two excited states.

Several excited electronic states of the ion have been accessed by optical transitions and characterized spectroscopically. The rotational detail allowed for the determination of the bond length in the vibrationless ground state of the ion, $r_e = 2.710 \pm 0.005 \text{ \AA}$. The ground state exhibits and the spectra are consistent with an $\Omega'' = 3/2$ electronic state. Long excited state-vibrational progressions allows extensive

characterization of upper states. The c state of the ion, for example, is now known to have an electronic origin at $T_{00} = 15550 \text{ cm}^{-1}$, a vibrational frequency of $\omega_e = 72.6 \text{ cm}^{-1}$, an anharmonicity of $\omega_e x_e = -0.811 \text{ cm}^{-1}$, an equilibrium rotational constant of $B_e = 0.0660 \text{ cm}^{-1}$ and a rotation-vibration constant of $\alpha_e = 0.00155 \text{ cm}^{-1}$. The zero point bond length of this state is $r_0 = 3.038 \pm 0.01 \text{ \AA}$ and it is bound (diabatically) by $1170 \pm 20 \text{ cm}^{-1}$. Assignment of the c-X band convergence at 16765 cm^{-1} as dissociation into $\text{Zr}^+(\text{b } ^2\text{G}_{7/2}) + \text{Ar } (^1\text{S})$ atomic fragments places the adiabatic binding energy of ground state of ZrAr^+ at $D_0 = 2690 \pm 20 \text{ cm}^{-1}$. The nature of small transition-metal molecules makes their generation and isolation a difficult task, particularly if a reasonable number density of the sample is desired for optical studies. Analogous experiments aimed at the measurement of high resolution optical spectra of ions are further hampered by the space-charge limitations of the number density of such species. Nonetheless, with the improvements which have been made, rotationally resolved spectra of heavy transition-metal diatomic cations have been obtained.

The rotational structure of electronic spectra of transition-metal electrostatic complexes has also been under investigation¹⁹. The study of electronic, rotational, and vibrational transitions in these simple isolated molecules has provided quantum mechanical detail of the structure of the electrostatic 'bond'. The following study considers the geometric structure of a $\text{M}^+\cdot\text{Ar}$ diatomic complex on which charge-(induced-dipole) binding forces dominate. This study complements the characterization of complexes of argon with first-row transition-metal^{8,13,20} and alkali earth²¹ cations.

ZrAr^+ Photodissociation

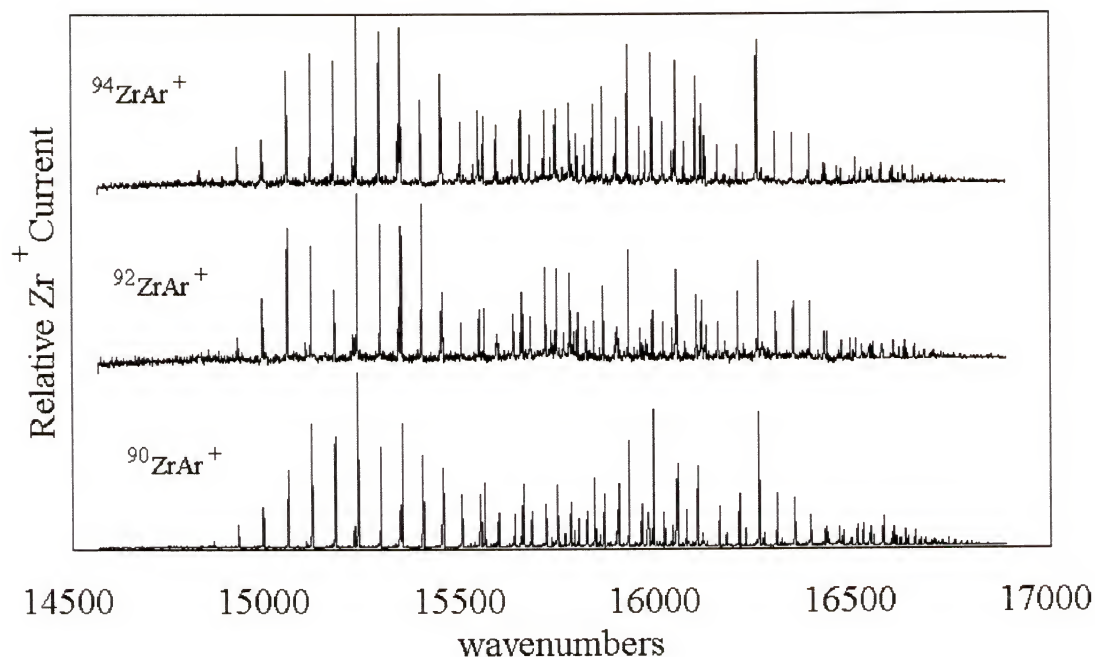


Figure 30. The ZrAr^+ Photodissociation for the Three Major Isotopes.

The figure shows resonant photodissociation spectrum with the three major isotopes (^{90}Zr 51.45%, ^{92}Zr 17.15% and ^{94}Zr 17.38%). There are five clear progressions here, with two which lead to a dissociation continuum.

ZrAr^+ Line Positions

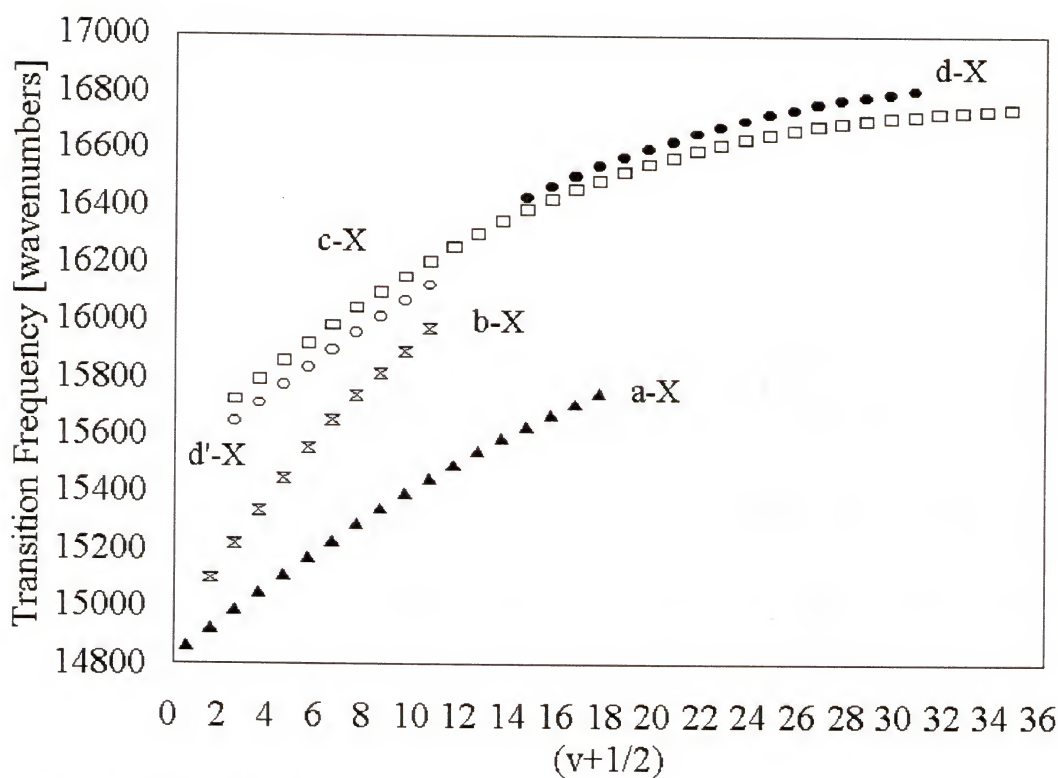


Figure 31. The ZrAr^+ Line Positions.

The figure shows the a-X, b-X, d'-X, c-X and d-X spin forbidden vibrational progressions for the ZrAr^+ cluster. The progressions d' and d appear to be part of the same progression but are split by the c progression, or are perturbed by the b state. The d'-X, c-X and d-X transitions are $\Delta\Omega = 1$. The a-X transitions are $\Delta\Omega = 0$ and the b-X transitions are $\Delta\Omega = -1$.

ZrAr^+ Rotational Structure Three States

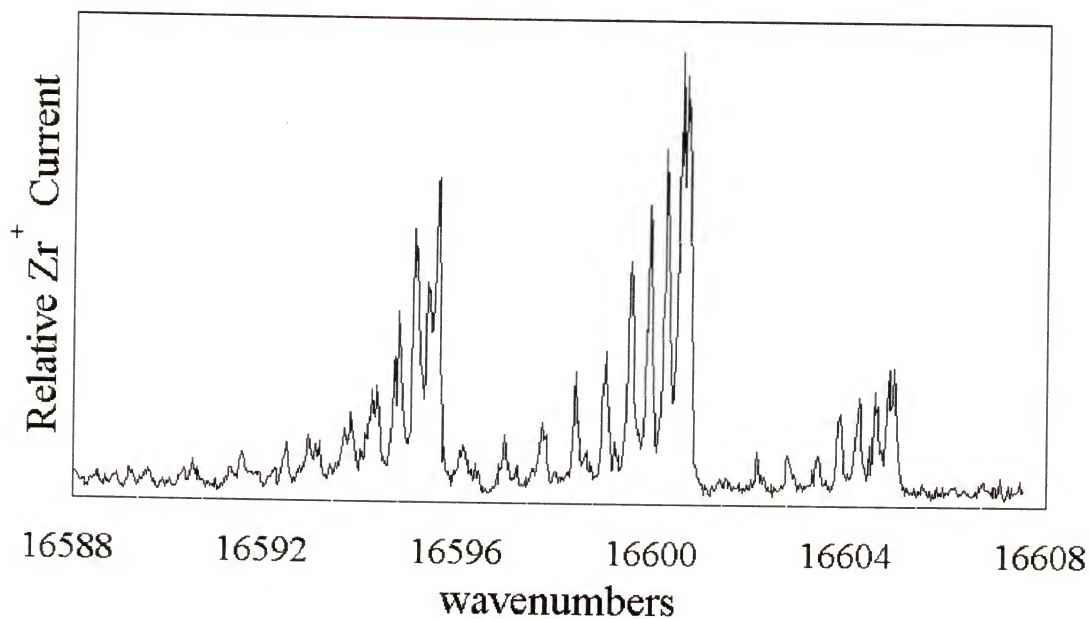


Figure 32. Rotational Scan of Three Separate ZrAr^+ Excited States.

The figure shows a high resolution scan of three ro-vibronic bands. The rotational detail shown in these three peaks is typical of the rest of the spectrum, but the exception for molecules of such high mass.

Figure 30 shows the ZrAr^+ photodissociation action spectrum over the region which has been scanned from ca. 14500 to 17000 cm^{-1} . There are five clear progressions which have been assigned as a, b, d', c and d to retain the notation of the previous work, and which are plotted in Figure 31. All transitions seen in this figure originate from $v''=0$, i.e. no "hot bands" are seen. This will be proven with rotational fits covering four different excited states, using the same ground state parameters. A blow up of several rotational resolved peaks is displayed in Figure 32, which displays three different excited state transitions.

Table VII lists the position of the vibronic bands observed for each of the excited state progressions. Fits to an anharmonic Morse potential give residuals which show that such a parameterization is accurate near the bottom of the potential, but fails near the top of the well, as expected for a charge induced-dipole bound ion. Simultaneous fits to the $^{94}\text{Zr}^{40}\text{Ar}^+$, $^{92}\text{Zr}^{40}\text{Ar}^+$, and $^{90}\text{Zr}^{40}\text{Ar}^+$ isotopomer spectra yield an absolute vibrational numbering for each transition. Table VIII lists the constants derived for these states of $^{90}\text{Zr}^{40}\text{Ar}^+$. All of these states have a larger internuclear separation than the zero-point level of the ground state because of the Franck-Condon factors which lead to the long vibrational progression and the red-degraded shape of each of the bands in the system. It is the rotational structure of these bands that enables the quantification of ground and excited state geometry.

Figure 33 shows a "blow-up" of a particularly well-resolved band, the (11,0), in the c-X transition with the three major isotopes. A portion of Figure 33 is replotted in Figure 34 with only the $^{90}\text{ZrAr}^+$ isotopomer experimental photodissociation spectrum

Table VII. ZrAr^+ a-X, b-X, d'-X, c-X and d-X Transitions Frequencies.

v	a-X	b-X	d'-X	c-X	d-X
0	14860.53				
1	14924.22	15098.17			
2	14987.43	15218.65	15644.89	15723.45	
3	15050.28	15335.23	15708.11	15790.86	
4	15111.50	15447.01	15770.66	15855.70	
5	15171.59	15552.87	15832.35	15920.09	
6	15230.01	15650.43	15893.19	15982.16	
7	15286.99	15736.81	15952.53	16043.01	
8	15341.76	15812.29	16010.16	16094.70	
9	15395.00	15889.82	16066.01	16149.81	
10	15445.54	15967.84	16119.60	16202.04	
11	15495.09			16251.84	
12	15541.67			16298.90	
13	15587.40			16343.60	
14	15629.17			16385.31	16428.95
15	15672.01			16423.08	16466.94
16	15708.11			16457.16	16503.53
17	15743.75			16488.77	16537.70
18				16518.25	16570.17
19				16545.17	16597.97
20				16567.90	16626.12
21				16593.04	16652.29
22				16613.65	16675.90
23				16631.91	16698.35
24				16649.93	16719.34
25				16665.07	16737.06
26				16678.57	16753.82
27				16690.92	16769.30
28				16701.85	16782.49
29				16711.30	16794.34
30				16718.59	16804.84
31				16725.81	
32				16730.14	
33				16736.52	
34				16740.79	

ZrAr⁺ Photodissociation

c-X Band (11,0)

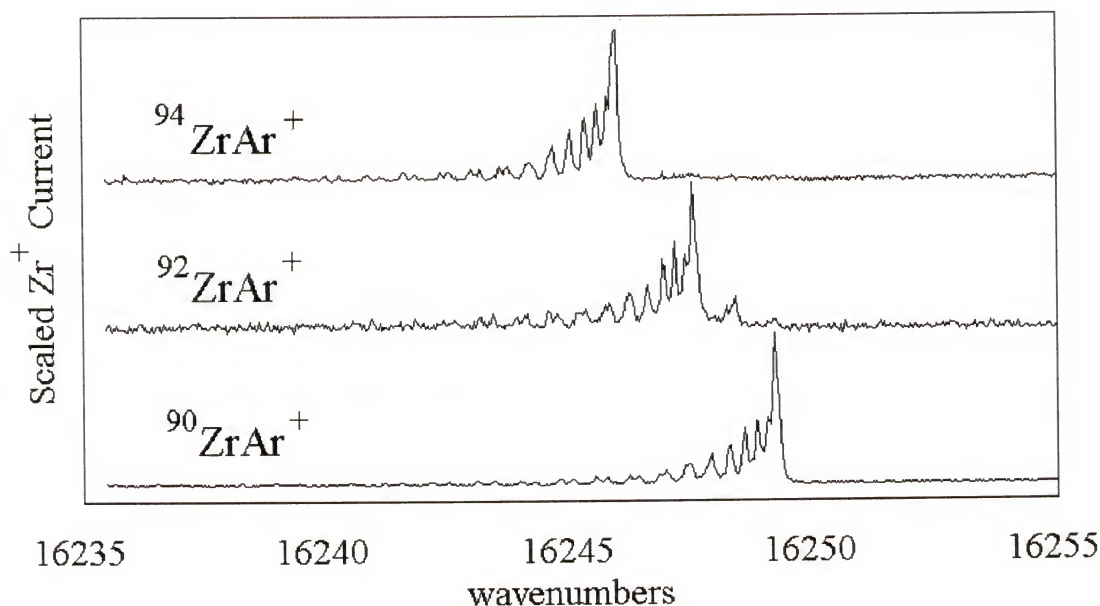


Figure 33. The ZrAr^+ c-X (11,0) Band with Three Major Isotopes.

The figure shows a high resolution scan of the c-X (11,0) ro-vibronic band with the three major isotopes (^{90}Zr 51.45%, ^{92}Zr 17.15% and ^{94}Zr 17.38%). This band is part of a $\Omega' = 5/2 - \Omega'' = 3/2$ ($\Delta\Omega = 1$, a perpendicular transition) system. The rotational fit of the major isotope $^{90}\text{ZrAr}^+$ is shown in another figure. The rotational resolution of these three peaks is amazing for a molecule of such high mass and for such small natural abundances for the $^{92}\text{ZrAr}^+$ and $^{94}\text{ZrAr}^+$.

$\text{ZrAr}^+ \text{ c-X (11,0) Transition}$

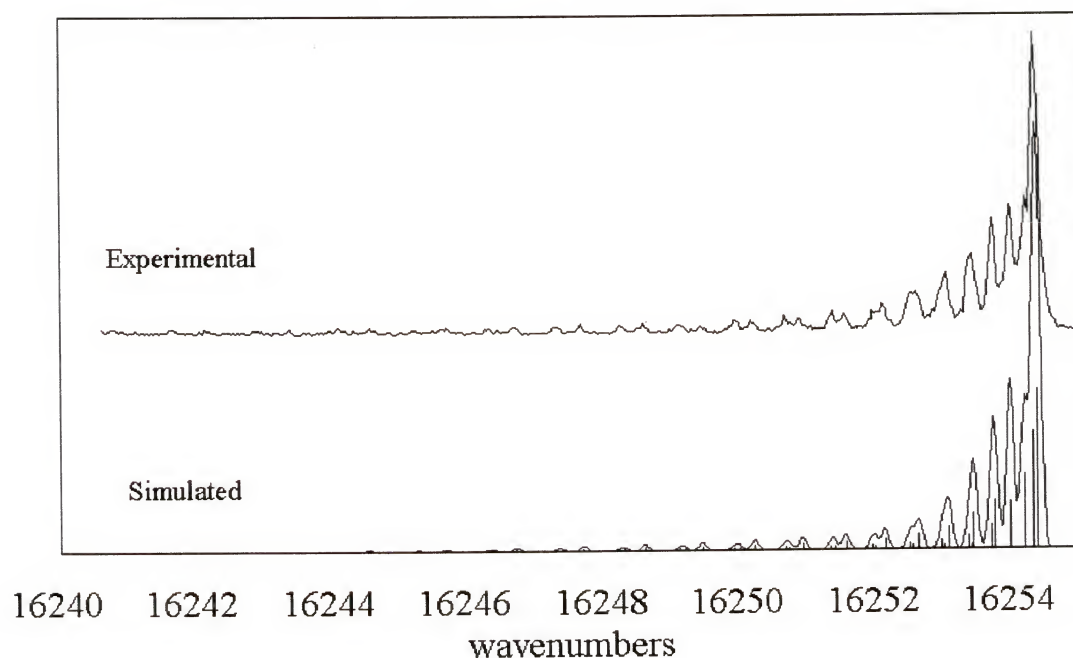


Figure 34. The $\text{ZrAr}^+ \text{ c-X (11,0)}$ Band.

The figure shows a closeup of the c-X (11,0) ro-vibronic band. This band is part of a $\Omega' = 5/2 - \Omega'' = 3/2$ ($\Delta\Omega = 1$, another perpendicular transition) system with a lower state rotational constant of 0.0829 cm^{-1} and an upper state rotational constant of 0.0489 cm^{-1} . The upper trace is the experimental spectrum and the lower trace is calculated with temperature lower than 2 K. The rotational resolution of this peak is amazing for a molecule of such high mass.

ZrAr^+ d'-X (8,0) Transition

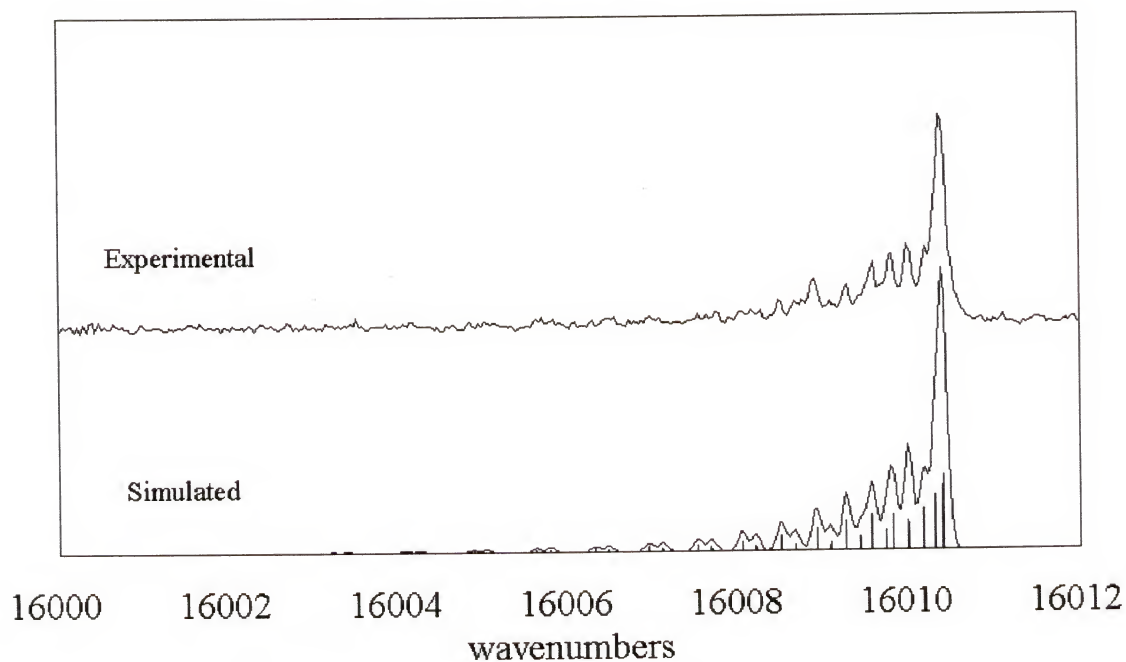


Figure 35. The ZrAr^+ d'-X (8,0) Band.

The figure shows a closeup of the d'-X (8,0) ro-vibronic band. This band is part of a $\Omega' = 5/2 - \Omega'' = 3/2$ ($\Delta\Omega = 1$, a perpendicular transition) system with a lower state rotational constant of 0.0829 cm^{-1} and an upper state rotational constant of 0.0551 cm^{-1} . The upper trace is the experimental spectrum and the lower trace is calculated with temperature lower than 2 K.

(upper trace) and a contour simulation (lower trace) under the assumption that the $^{90}\text{ZrAr}^+$ molecule is a rigid-rotor symmetric-top. The simulation is generated via convolution of a instrument function (Gaussian, FWHM= 0.07 cm^{-1} , about equal to the laser linewidth) with the calculated line positions and intensities to obtain a parameterized rotational band contour. The excellent agreement between the experimental and simulated spectrum indicates that the c-X system is an $\Omega' = 5/2 - \Omega'' = 3/2$ (perpendicular) transition with a large decrease in rotational constant upon excitation. The rotational constants determined from the fit of this band are $B'' = 0.0829\text{ cm}^{-1}$ for the ground state and $B' = 0.0489\text{ cm}^{-1}$ for the upper state which yields a vibrationally averaged bond length of $2.710\text{ \AA}$ and $3.528\text{ \AA}$ for those states respectively.

Table VIII. ZrAr^+ Spectroscopic Constants in cm^{-1} .

Constant	X	a	b	d'	c	d
T_{co}		14829	14911	15489	15550	15686
w_e		65.7	129	63.1	72.6	60.4
$w_e x_e$		-0.475	-2.17	0.212	-0.811	-0.42
$w_e y_e$		-0.0164		-0.0457	-0.0149	-0.0139
D					16765	16869
D_e	2690 ⁱ				1215	1183
B_e	0.0829				0.0660	
α_e					0.00155	

ⁱ $D_0 \pm 20\text{ cm}^{-1}$.

Figure 35 shows a closeup of a band from another system, the d'-X (8,0). The fit of this band indicates that this system, too, is a $\Delta\Omega = 1$ transition from the same

$\Omega'' = 3/2$ ground state as in the previous fit. Here the rotational constants obtained from the fit are $B'' = 0.0829 \text{ cm}^{-1}$ for the ground state and $B' = 0.0551 \text{ cm}^{-1}$ for the upper state indicating as an upper state bond length of $3.324 \text{ \AA}$. Since the ions in the beam are vibrationally and electronically cold, all the bands must (and do) show a consistent value of lower rotational constant.

Figure 36 shows a closeup of a band from another system, the a-X (14,0). The fit of this band indicates that this system is a $\Delta\Omega = 0$ (parallel) transition from the same $\Omega'' = 3/2$ ground state. Here the rotational constants obtained from the fit are $B'' = 0.0829 \text{ cm}^{-1}$ for the ground state and $B' = 0.0504 \text{ cm}^{-1}$ for the upper state indicating as upper state bond length of $3.475 \text{ \AA}$.

Figure 37 shows a closeup of a band from another system, the d-X (20,0). The fit of this band indicates that this system is another $\Delta\Omega = 1$ (perpendicular) transition from the same $\Omega'' = 3/2$ ground state. Here the rotational constants obtained from the fit are $B'' = 0.0829 \text{ cm}^{-1}$ for the ground state and $B' = 0.0344 \text{ cm}^{-1}$ for the upper state indicating as upper state bond length of $4.207 \text{ \AA}$.

The b-X state has interesting rotational structure to the blue of the rotational band origin. The appearance of these blue features seems to indicate a $\Delta\Omega = -1$ transition. A best fit to a b-X (7,0) is shown in **Figure 38**. The same ground state as the previous fits was used with an upper state rotational constant of $B' = 0.0656 \text{ cm}^{-1}$ to obtain the fit.

The consistency of the ground state rotational constant for each of these excited state rotational bands is convincing. The proof of this is that many of the c-X transitions and several of the other transitions have all been fit to the same vibrationless ground state

rotational constant. In fact the rotational constants for the c excited state, **Figure 39**, plotted against the vibrational quantum number, as in equation (4), to reveal the equilibrium rotational constant of $B_e = 0.0660 \text{ cm}^{-1}$ and a rotation-vibration constant of $\alpha_e = 0.00156 \text{ cm}^{-1}$.

More information is yielded in the rotational contour than just the rotational constants. The simulation of the spectrum generated is admittedly crude, a rigid symmetric top simulation, and thus the branch intensities are expected to be somewhat inaccurate, but the comparison with the observed spectrum yields an estimate of the rotational temperature of the ions in our beam: $<2 \text{ K}$. However, the lower panel in each of the figures has been generated with a rotational distribution not described by a single Boltzmann but a composite of 95% (1.5 K) ions and 5% (15 K) ions. This seems to adequately fit the high J 'tail' to the band shape. This 'tail' may be the result of the 'freezing in' of rotational energy as the collision energy drops during supersonic expansion and has been observed before in the spectra of CoAr^+ . Nonetheless, this ion appears to be slightly rotationally colder than other ions such as Ni_2^+ which is discussed in Chapter 5.

LeRoy-Bernstein analysis¹¹ of the vibrational structure of the upper states in an electronic transition yields the diabatic dissociation of that state. This treatment shows that a diatomic molecule will exhibit vibrational structure near dissociation that is determined by the long-range attractive force between the separated atoms. For ZrAr^+ , this force is charge-(induced-dipole) and scales like $1/r^4$. In this case, a plot of $(\{G(v'+1) - G'(v'-1)\}/2)^{4/3}$ versus transition frequency is linear near dissociation and may be used to confidently extrapolate experimental band origins to the convergence. This is the same

ZrAr^+ a-X (15,0) Transition

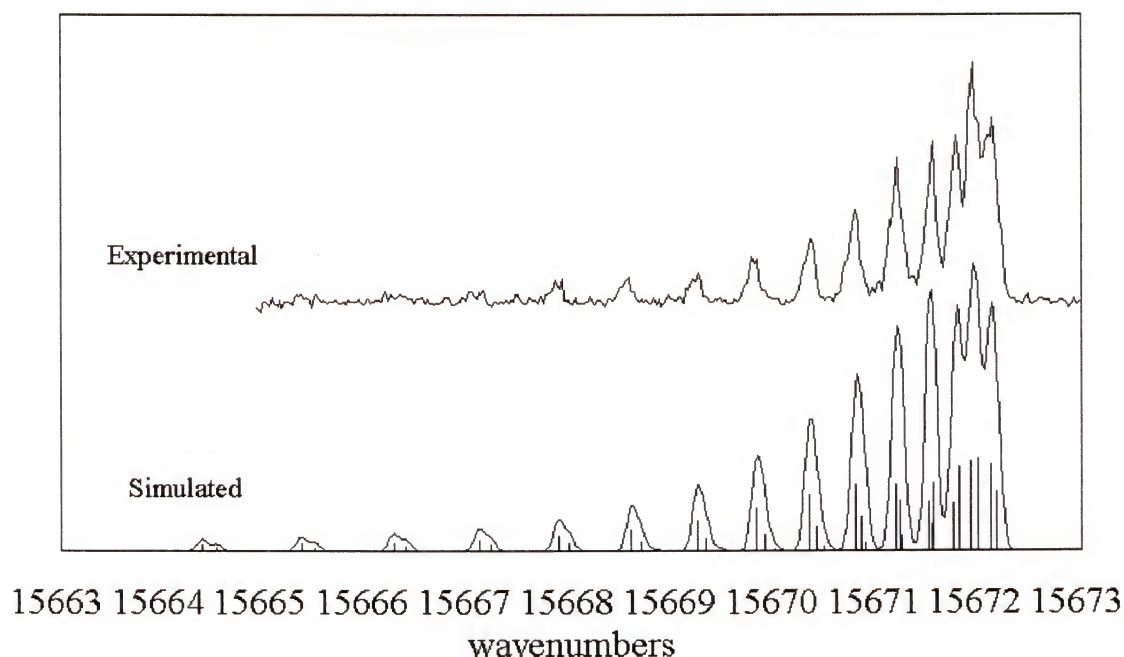


Figure 36. The ZrAr^+ a-X (15,0) Band.

The figure shows a closeup of the a-X (15,0) ro-vibronic band. This band is part of a $\Omega' = 3/2 \leftarrow \Omega'' = 3/2$ ($\Delta\Omega = 0$) system with a lower state rotational constant of 0.0829 cm^{-1} and an upper state rotational constant of 0.0504 cm^{-1} . As in previous rotational plots, the upper trace is the experimental spectrum and the lower trace is calculated with temperature lower than 2 K.

ZrAr^+ d-X (20,0) Transition

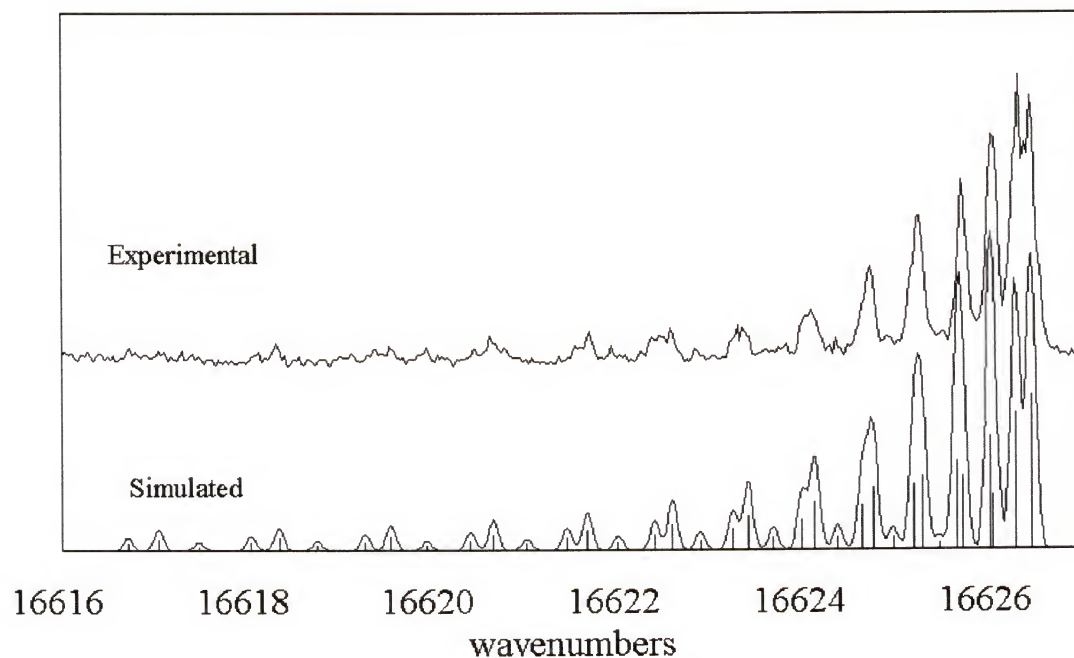


Figure 37. The ZrAr^+ d-X (20,0) Band.

The figure shows a closeup of the d-X (20,0) ro-vibronic band. This band is part of a $\Omega' = 5/2 - \Omega'' = 3/2$ ($\Delta\Omega = 1$) system with a lower state rotational constant of 0.0829 cm^{-1} and an upper state rotational constant of 0.0344 cm^{-1} . The upper trace is the experimental spectrum and the lower trace is calculated with temperature lower than 2 K. With four rotational states fit with the same ground state rotational constant the possibility of misassigning these upper state rotational constants is significantly diminished.

procedure which has been applied to assigned dissociation limits of the CoAr^+ and NiAr^+ discussed in a previous section. A more sophisticated treatment has recently been performed for the MgAr^+ cluster²²²². Values of 16765 and 16866 cm^{-1} are observed on this study for the diabatic dissociation limit for the c and d states of ZrAr^+ respectively and are displayed in Figure 40. These limits are identified as the dissociation into $\text{Zr}^+(\text{b } ^2\text{G}_{7/2}) + \text{Ar}(^1\text{S})$ atomic fragments and $\text{Zr}^+(\text{b } ^2\text{D}_{7/2}) + \text{Ar}(^1\text{S})$ from the separation between the two states 101 cm^{-1} . The ground state adiabatic dissociation limit of ZrAr^+ is calculated from the observed limit and the known energy levels of the Zr^+ ion¹² to be $D_0 = 2690 \pm 20 \text{ cm}^{-1}$.

The ground state of ZrAr^+ , or any other state of the ion for that matter, has not been assailed by *ab initio* theory. The ground state of a lighter analog to this molecule, TiAr^+ , has been studied theoretically, however. Bauschlicher et al.⁹, predicts a $^4\phi(\text{d}^2\text{s})$ ground state for TiAr^+ , with a binding energy of $D_0 = 0.218 \text{ eV}$ (1760 cm^{-1}) and an average internuclear separation of 2.709 Å.

Experimentally the binding energy predicted by theory is found to be systematically 20% too low for first-row transition-metal argon complexes. Nonetheless, the bond length calculated for these molecular ions may compare well with experiment. If the calculation for the isovalent TiAr^+ is compared with that of the experimental results for ZrAr^+ , the bond length predicted is only slightly shorter than experimental but the binding energy is significantly (35%) low, perhaps consistent with a trend. What is the cause of the error on predicted binding energies? Will the second-row transition metal ion complexes follow the same 'scale factor' for bonding energies as the first-row ions? What

ZrAr^+ b-X (7,0) Transition

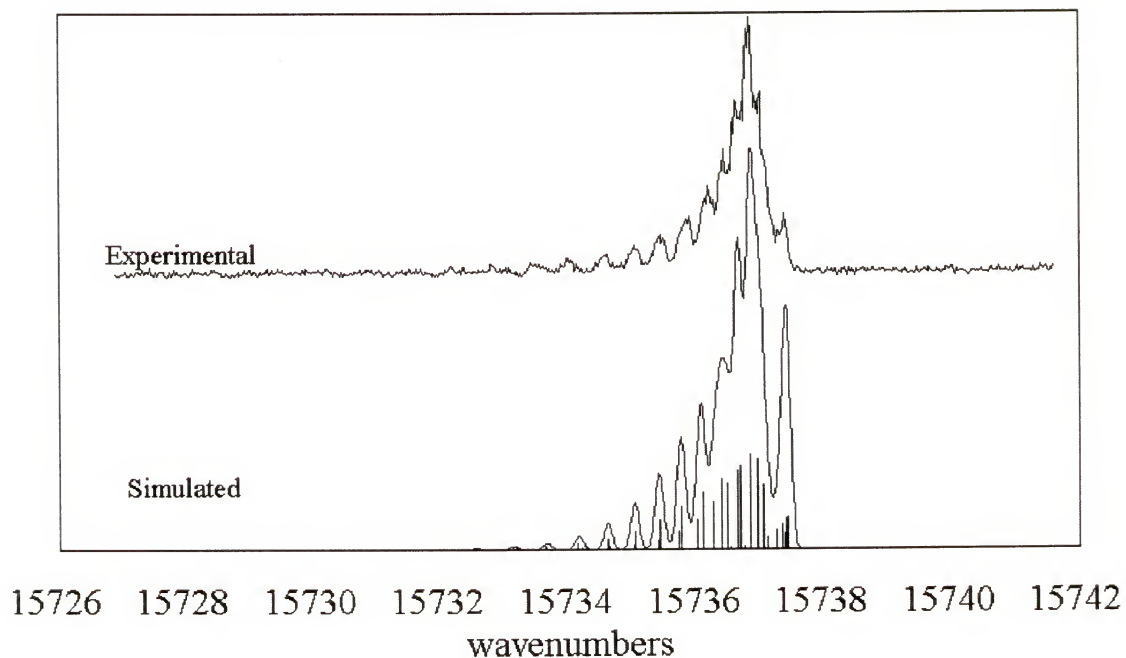


Figure 38. The ZrAr^+ b-X (7,0) Band.

The figure shows a closeup of the b-X (7,0) ro-vibronic band. This band is part of a $\Omega' = \frac{1}{2} \leftarrow \Omega'' = \frac{3}{2}$ ($\Delta\Omega = -1$, a perpendicular transition) system with a lower state rotational constant of 0.0829 cm^{-1} and an upper state rotational constant of 0.0656 cm^{-1} . The upper trace is the experimental spectrum and the lower trace is calculated with temperature lower than 2 K.

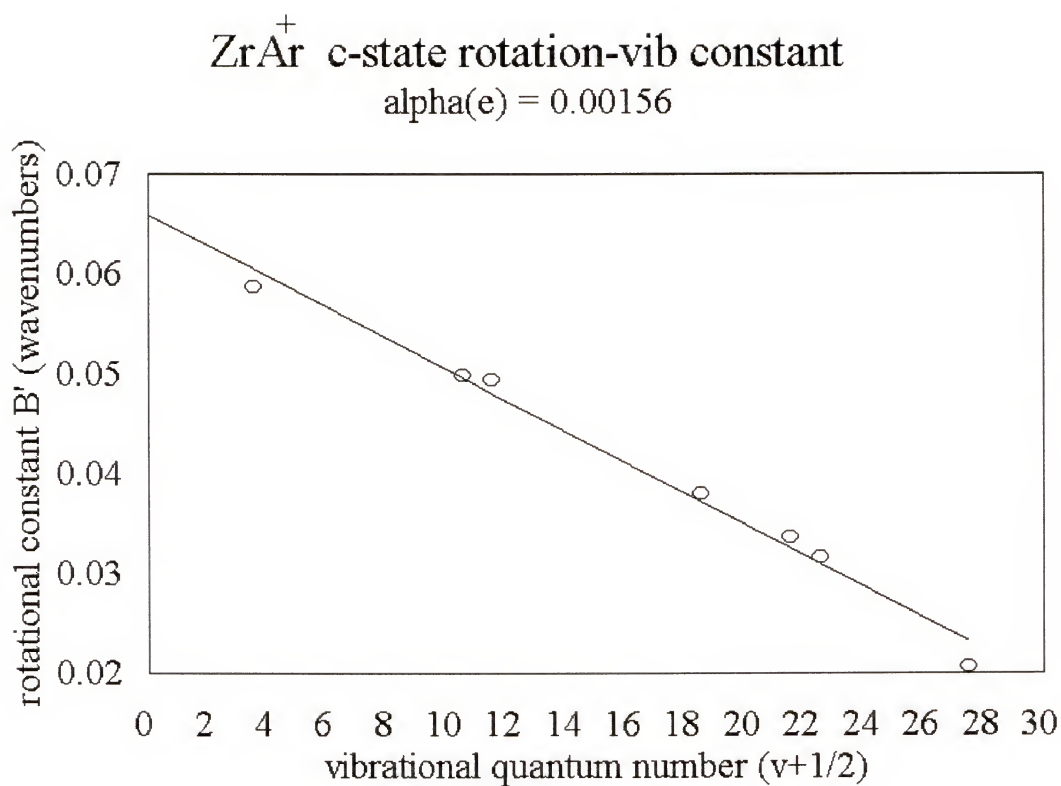


Figure 39. ZrAr Rotational Constants versus Vibrational Quantum Number.

The figure shows ZrAr^+ c state rotational constant versus vibrational quantum number. The fit of the rotational constant versus vibrational number gives α_e , how fast the bond length changes with vibrational quantum number. The rotational constants have been extracted from rotational fits to high resolution scans of the ZrAr^+ c state.

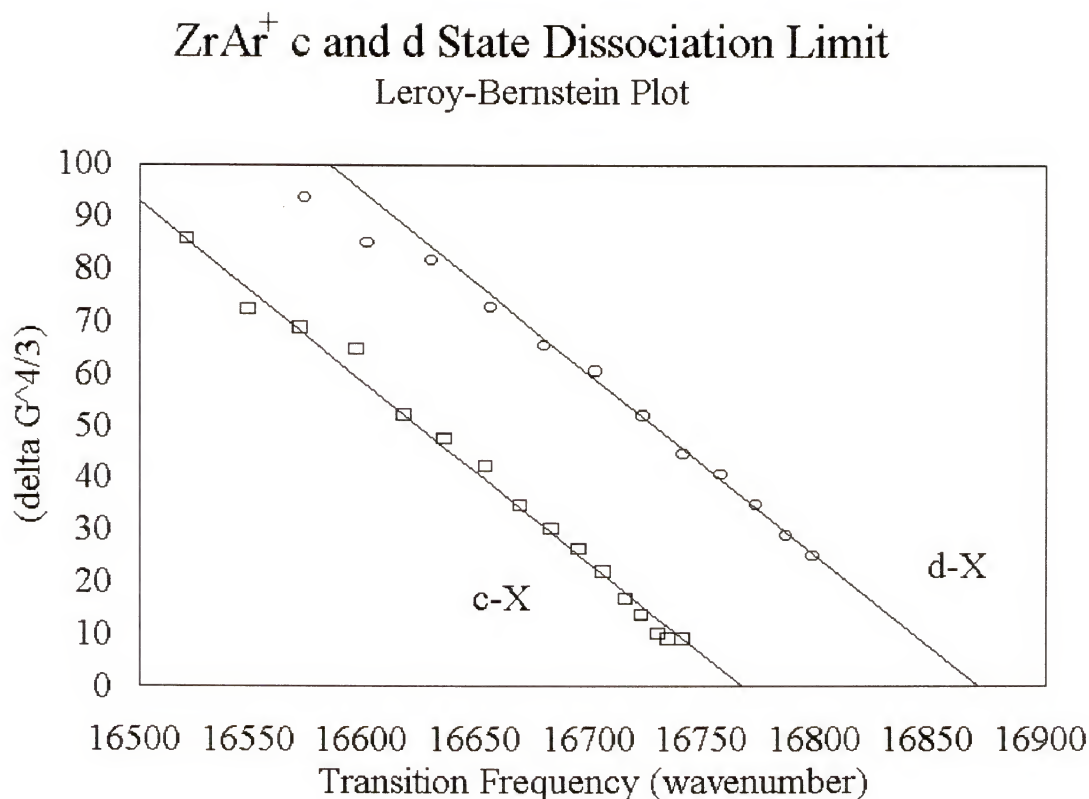


Figure 40. ZrAr⁺ c and d State LeRoy-Bernstein Fit.

The figure shows dissociation limits from the c and d state LeRoy-Bernstein fit. The plot of the derivative of the $\Delta G'(v')^{4/3} = [\{G'(v'+1) - G'(v'-1)\}/2]^{4/3}$ versus transition frequency for the observed energy levels. The c and d state dissociation limits occur at 16765 and 16866 cm⁻¹ respectively. These arise from the Zr⁺(b ²G_{7/2})+Ar(¹S) and Zr⁺(b ²D_{7/2})+Ar(¹S) atomic fragments, assigned by the difference in the dissociation limits of 101 cm⁻¹.

is the role of spin-orbit coupling in the description of the states of these molecules? These questions remain to be answered, since this is the first second row transition metal ion bound to argon to be investigated. The role of spin-orbit coupling is hoped to be found in the xenides of the transition metal cations.

Cobalt Xenon Cation

The CoXe^+ system is of interest because it is the next rare-gas in the series since CoAr^+ and CoKr^+ ions have been studied⁸. Several attempts have been made to produce the CoNe^+ , but proper conditions have not yet been obtained. CoHe_n^+ ($n=1$ to 8) have been produced and observed in our mass spectrometer, however, the CoHe^+ optical spectrum has not been observed. This is in part due to the small daughter/parent ion ratio of $\text{Co}^+/\text{CoHe}^+$. CoXe^+ does not have these problems. A 0.1% Xe in He tank produces sufficient amounts to observe the photodissociation action spectrum with good signal-to-noise ratio. The binding of the xenide is expected to be higher than the argide or kryptide because the polarizability²³ is larger ($\alpha_{\text{Ne}}=0.397\text{\AA}^3$, $\alpha_{\text{Ar}}=1.67\text{\AA}^3$, $\alpha_{\text{Kr}}=2.52\text{\AA}^3$, $\alpha_{\text{Xe}}=4.11\text{\AA}^3$), and therefore the magnitude of charge induced dipole interaction as well.

The size of the polarizability tells only part of the story, since the binding energy is also dependant upon the bond length. For the argide and kryptide, the size of the atom allows the rare-gas to get into the d-holes of the Co^+ ion. Xenon is so large that it precludes this type of overlap. Figure 41 shows an overview of the spectrum. Four of the states present have been assigned from their isotope shifts and the vibrational progressions which are displayed in Figure 42. Several more states are clearly present but

CoXe^+ Photodissociation

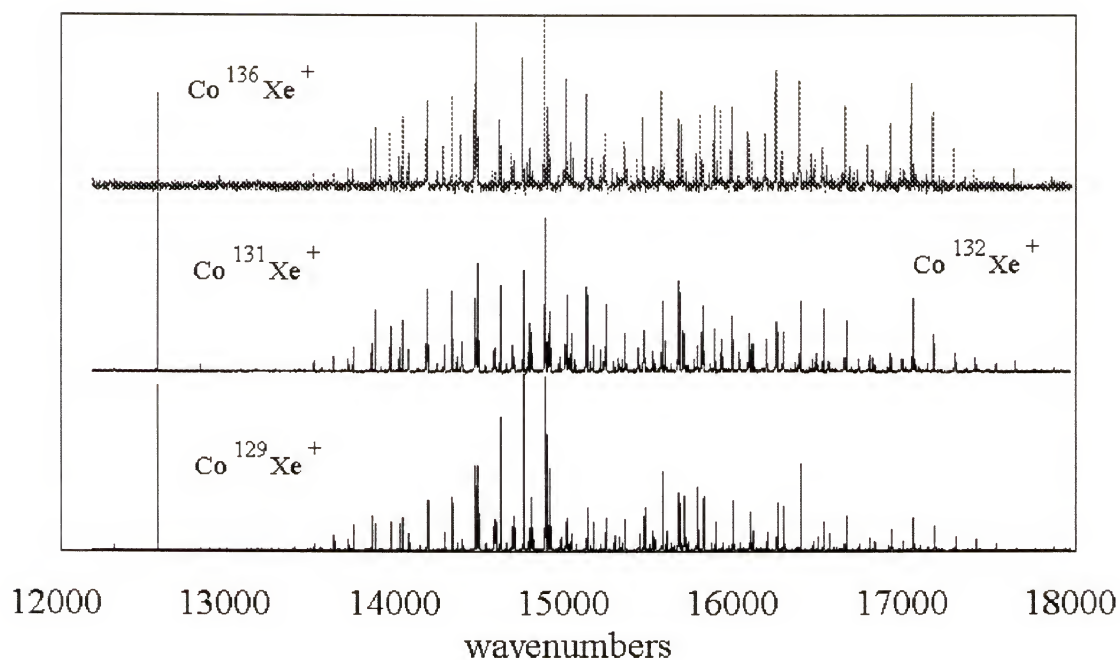


Figure 41. CoXe^+ Photodissociation Spectrum.

The figure shows three traces of the CoXe^+ photodissociation spectrum. The top trace is the Co^+ current from $\text{Co}^{136}\text{Xe}^+$, the middle is a mixture of the Co^+ from $\text{Co}^{131}\text{Xe}^+$ and $\text{Co}^{132}\text{Xe}^+$, and the bottom trace is from $\text{Co}^{129}\text{Xe}^+$. In the figure, at least four electronic transitions are observed. Currently these are assigned labels a, A, B, C, D and E. There are several unassigned peaks in the spectrum and there is significant perturbation of many of the peaks which appear.

CoXe^+ Isotope Shifts

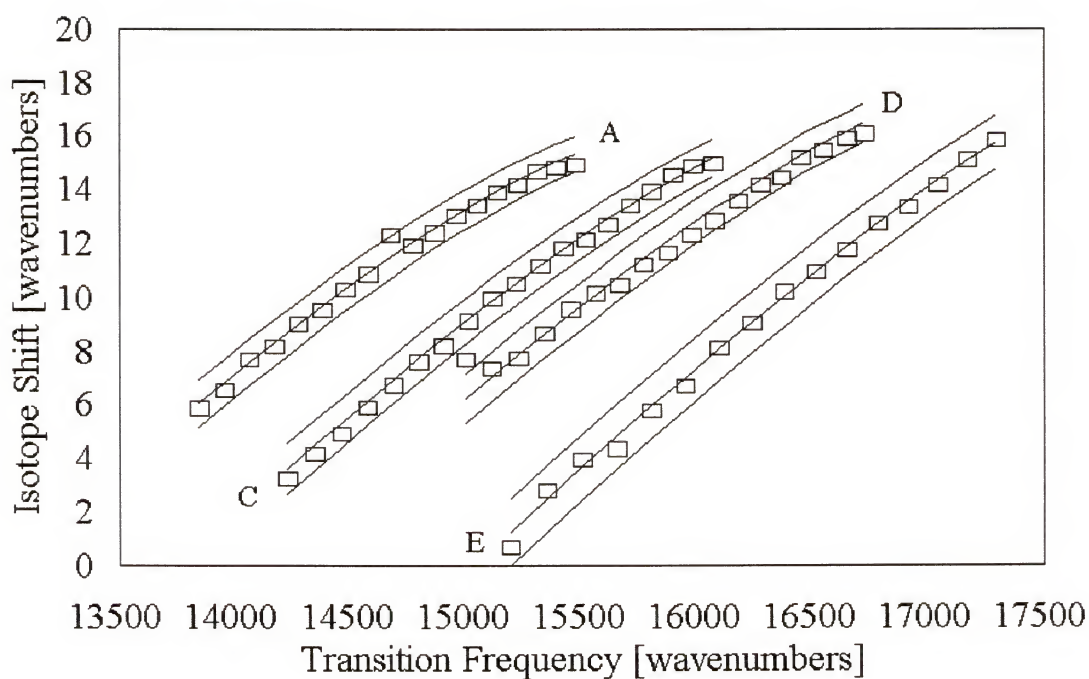


Figure 42. CoXe^+ A-X, C-X, D-X and E-X Transitions versus Isotope Shifts.

The figure shows transition frequencies versus isotope shift for four assigned states in the CoXe^+ spectrum. The symbols are the observed line positions versus the lines and isotope shift. The calculated isotope shift versus line positions are plotted as lines. The line above and below the symbols are plus and minus one vibrational quanta. The line through the symbols corresponds to the correct assignment of the vibrational quanta.

have as yet remained unassigned. One additional state has been assigned as the a state from the position, isotope shift and line shape, which are similar to the CoAr^+ a state and the $\text{Co}^+\cdot\text{CO}_2\tilde{\text{A}}$ state, the rotational contour is displayed in **Figure 43**.

Several details have been revealed about the CoXe^+ system, however, it clear that this system requires further investigation. The larger polarizability seems to contribute to a significantly larger photodissociation cross section (as compared to the CoAr^+ cluster). The role of spin-orbit contributions is not clear at this point. Perhaps the most interesting feature of this cluster is the similarity of the a state to that found in the CoAr^+ cluster and very recently in the CoKr^+ cluster. This state, while not fully rotationally resolved in the CoXe^+ cluster, has been fit well, to give both an ground and upper state r_0 . The bond lengths of this cluster are slightly larger than the CoAr^+ . The newly observed CoKr^+ a state is fully resolved, which helped confirm the identity of the state, and has a bond length which lies between the two as might be expected. Identification of the other states in this system appears to be relatively straight forward with only a little more work. Rotational analysis for large v' of CoXe^+ would most likely provide new and useful information.

CoXe^+ a-X (0,0) Transition

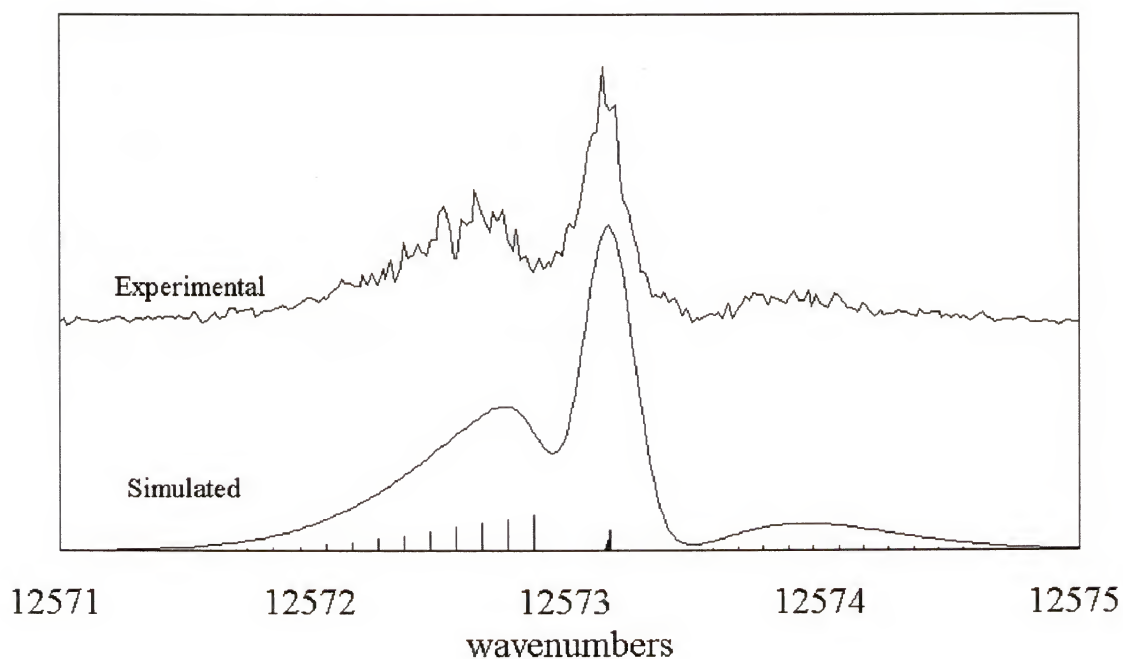


Figure 43. The CoXe^+ a-X (0,0) Band.

The figure shows a closeup of the spin forbidden a-X (0,0) origin band in $\text{Co}^{129}\text{Xe}^+$. This band is part of a $\Omega' = 2 - \Omega'' = 3$ system as was the CoAr^+ a-X(0,0) origin, but with a $B'' = 0.0502 \text{ cm}^{-1}$ an upper state exhibiting a rotational constant $B' = 0.0501 \text{ cm}^{-1}$. This indicates only a small change in geometry from the ground electronic state to the excited state. Again the upper trace is the experimental spectrum and the lower trace is calculated with a rotational temperature of $\approx 2.4 \text{ K}$.

CHAPTER 4

ONE-COLOR PHOTODISSOCIATION OF POLYATOMICS

Gas-phase analysis of molecular clusters provides a unique and powerful way to study intermolecular interactions typically found in condensed phases. Choosing systems which are chemically interesting and yet simple enough to be tractable has been the goal of our research group for the past several years. Previously we have discussed several transition-metal cations bound to rare-gas adducts. These systems have given considerable understanding of the charge induced-dipole forces which dominate their bonding. Large polyatomic clusters have been an enigma. This is because the number of modes built upon the electronic transition arising from the transition metal chromophore increases linearly with number of atoms.

Cobalt Carbon Dioxide Cation

The dynamics of ion recombination in size-selected CO_2 clusters have been used to probe solvation dynamics in the time domain.²⁴ Interpretation of the experimental data requires simulation which requires an *a priori* potential for the ion- CO_2 interaction. The photodissociation experiment performed on the CoCO_2^+ cluster gives an experimental benchmark on which these electrostatic potentials can be based. This is the most

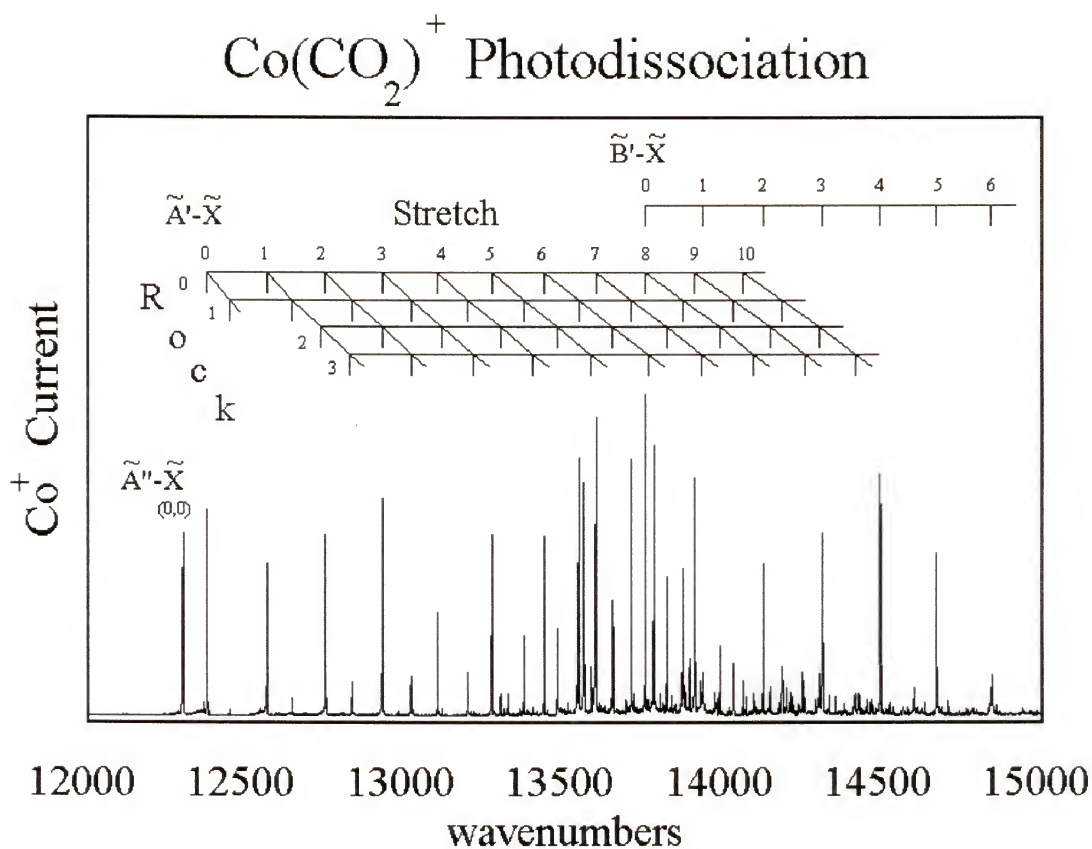


Figure 44. CoCO_2^+ $\tilde{\text{A}}''$, $\tilde{\text{A}}'$ and $\tilde{\text{B}}$ States.

The figure shows a portion of the resonant photodissociation spectrum of CoOCO^+ in the region of 12000 to 15000 wavenumbers. The horizontal axis is the dissociation laser frequency and the vertical axis is relative Co^+ photocurrent resulting from the fragmentation of mass selected CoOCO^+ . Three electronic transitions are seen in this spectrum, which are labeled $\tilde{\text{A}}''$ - $\tilde{\text{X}}$, $\tilde{\text{A}}'$ - $\tilde{\text{X}}$ and $\tilde{\text{B}}'$ - $\tilde{\text{X}}$ in correspondence to similarly defined labels of transitions in CoAr^+ .

$\text{Co}(\text{CO}_2)^+$ Photodissociation

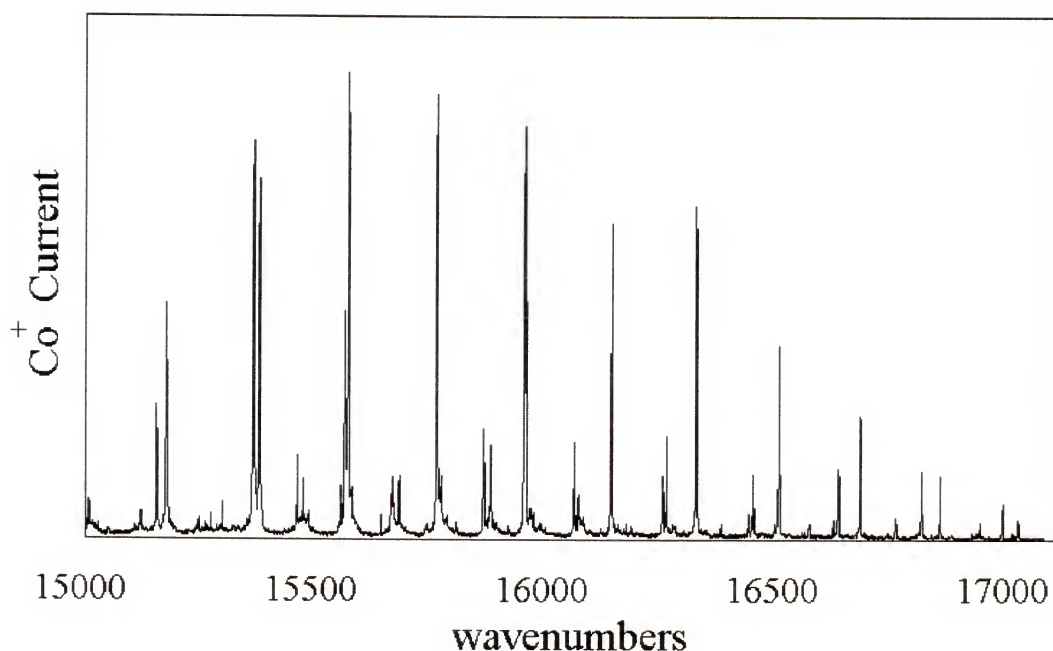


Figure 45. CoCO_2^+ $\tilde{\text{B}}$ and $\tilde{\text{C}}$ States.

The figure shows a portion of the resonant photodissociation spectrum of CoOCO^+ in the region of 15000 to 17100 wavenumbers. The horizontal axis is the dissociation laser frequency and the vertical axis is relative Co^+ photocurrent resulting from the fragmentation of mass selected CoOCO^+ . Two electronic transitions are seen in this spectrum which are labeled $\tilde{\text{B}}-\tilde{\text{X}}$ and $\tilde{\text{C}}-\tilde{\text{X}}$ in correspondence to similarly defined labels of transitions in CoAr^+ .

reasonable hope for correct modeling of the many-body potential of a finite cluster or in an infinite electrolytic solution.

The resonant photofragmentation spectrum of CoCO_2^+ has been obtained for the range of 12000 to 17100 cm^{-1} shown in **Figure 44** and **Figure 45**. These figures show the only observed photofragmentation pathway at these photon energies:



which is the reverse of the formation process. The features of this spectrum are similar to the previously discussed CoAr^+ , CoXe^+ and CoH_2O^+ spectra and the published results for the CoAr^+ and CoKr^+ spectra⁸. The resonant absorptions of this ion result from more than one electronic transition and therefore more than a single set of vibrational transitions.

The complexity of the electronic states at this energy above the electronic ground state is merely a result of the numerous low-lying electronic states of the Co^+ ion. To date, six electronic transitions in the CoAr^+ cluster ion have been characterized and labeled in increasing order of electronic origin $\tilde{\text{A}}'$, $\tilde{\text{a}}$, $\tilde{\text{B}}'$, $\tilde{\text{B}}$ and $\tilde{\text{C}}$. In order to remain consistent with previous nomenclature of the original work on CoAr^+ spectra⁸, this unfortunate choice of labels has been preserved in the labeling of the CoOCO^+ states. The list of the 40 assigned transitions which have been labeled as the $\tilde{\text{A}}'$ state in **Figure 44** are given in **Table IX**.

These bands have been assigned to a progression of stretching and rocking motions on a single excited electronic surface, the $\tilde{\text{A}}'$ state. All of these bands are cold, meaning each

Table IX. CoOCO⁺ band origins for the $\tilde{A}'-\tilde{X}$ electronic transitions.

Observed	Obs-Calc	v_S	v_R	Observed	Obs-Calc	v_S	v_R
12373.55	-0.81	0	0	12728.49	1.83	1	2
12561.91	-0.05	1	0	12922.02	1.05	2	2
12745.16	0.37	2	0	13109.62	-0.36	3	2
12923.59	0.57	3	0	13293.09	-0.74	4	2
13097.85	1.06	4	0	13472.06	-0.60	5	2
13267.02	0.77	5	0	13646.13	-0.50	6	2
13431.76	0.20	6	0	13816.10	0.21	7	2
13592.64	-0.22	7	0	13981.29	0.71	8	2
13749.71	-0.58	8	0	14141.29	0.43	9	2
13902.83	-1.17	9	0	14296.54	-0.32	10	2
14053.90	-0.27	10	0	14447.05	-1.71	11	2
14200.33	-0.58	11	0	12821.30	-0.91	1	3
14345.09	0.69	12	0	13019.59	-0.03	2	3
12444.90	0.29	0	1	13211.39	0.04	3	3
12638.83	-0.35	1	1	13397.14	-0.43	4	3
12828.27	-0.38	2	1	13578.94	0.51	5	3
13012.44	-0.72	3	1	13754.31	0.23	6	3
13191.81	-1.04	4	1	13926.14	1.48	7	3
13367.28	-0.61	5	1	14089.18	-1.14	8	3
13538.15	-0.26	6	1	14251.02	-0.19	9	3
13704.62	0.05	7	1	14407.49	0.00	10	3
13866.79	0.27	8	1	14559.74	0.44	11	3
14025.26	0.86	9	1				
14180.13	1.76	10	1				
14328.78	0.20	11	1				
14475.11	-0.06	12	1				

Table X. CoOCO⁺ Spectroscopic Parameters with Various Fits.

Parameters	9 Parameter Fit	7 Parameter Fit	5 Parameter Fit
T_{00}	12374.36	12375.80	12366.81
ω_s	190.02	187.98	191.10
ω_R	63.53	65.41	84.78
x_{SS}	-2.45	-2.01	-2.20
x_{RR}	7.08	5.54	0.35
x_{SR}	8.04	8.00	3.29
y_{SSR}	-0.18	-0.18	
y_{SRR}	-0.89	-0.90	
y_{SSS}	0.02		
y_{RRR}	-0.36		

transition is excited from the vibrationless ground state. The vibrational structure in this state gives evidence of a significant equilibrium geometry change between the ground $\tilde{X}$ and excited $\tilde{A}'$ electronic state.

The $\tilde{A}'$ - $\tilde{X}$ band origin has been analyzed with respect to the simple series expansion³ for the energies of an anharmonic oscillator of more than one degree of freedom:

$$\frac{E}{hc} = T_0 + \sum_i \omega_i v_i - \sum_i \sum_{j>i} x_{ij} v_i v_j + \sum_i \sum_{j>i} \sum_{k>j} y_{ijk} v_i v_j v_k + \dots \quad (7)$$

where the i, j and k indices label the normal mode numbering, v_i label the vibrational quanta and ω_i , x_{ij} and y_{ijk} refer to vibrational frequencies and first- and second- order

anharmonicities. (Note that this expression hides a multitude of sins associated with the zero point energy of each mode. This will have to be accounted for in the full normal mode analysis.) If the cluster is rigid enough for a separation of rotational and vibrational motion, there are $3N-6=6$ normal modes of vibration. Four of these modes originate from the CO_2 degrees of freedom: ν_1 , the symmetric O-C-O stretch, ν_2 , the degenerate Δ OCO bend (which splits into two modes: an in-plane and an out-of-plane mode), and ν_3 , the asymmetric O-C-O stretch. The vibrational modes which correspond to the complexation are ν_s , the $\text{Co}^+ \leftrightarrow (\text{OCO})$ stretching mode and ν_r , the rigid $\text{Co}^+ \triangleleft (\text{OCO})$ rock with respect to the metal ion. There is no activity in any of the intrinsic CO_2 normal motions in this electronic transition. For the two complex modes, five vibrational constants are needed to describe the spectrum to first order: ω_s , the $\text{Co}^+ \leftrightarrow (\text{OCO})$ stretching frequency; ω_r , the $\text{Co}^+ \triangleleft (\text{OCO})$ rigid rocking frequency; x_{ss} , the diagonal stretching anharmonicity; x_{rr} , the diagonal rocking anharmonicity; and x_{sr} , the cross anharmonicity between the stretch and rock. The last constant, x_{sr} , may be interpreted as the amount that excitation in the rocking motion weakens (or, in this case, strengthens) the 'effective' stretching force constant. Fits of the 40 band positions to just these five constants show a systematic deviation between observed and calculated line positions. Therefore, these constants alone fail to describe the potential surface for this complex. The simplest successful form that fits the experimental band positions contains 2 second-order (y_{ijk}) parameters:

$$v[A'(v_s, v_r) - X(0,0)] = T_{00} + \omega_s v_s + \omega_r v_r - x_{ss} v_s^2 - x_{rr} v_r^2 - x_{sr} v_s v_r + y_{ssr} v_s^2 v_r + y_{srr} v_s v_r^2 \quad (8)$$

where v_s and v_R are the stretch and rock upper state vibrational quantum numbers, T_{00} is the electronic origin, ω_s and ω_R are the stretch and rock harmonic frequencies, x_{ss} , x_{RR} and x_{sR} are the first order anharmonicity constants, and y_{ssR} and y_{sRR} are the second order anharmonicity constants. Extensive testing of the data set to formula of the type indicates that this is the smallest number of parameters which fit the spectrum without significant systematic deviation. The RMS deviation of the fit to equation (8) to the data in Table IX is 1.1 cm^{-1} , slightly above estimated experimental error in the band positions. A nine parameter fit gives a slightly better RMS deviation and smaller coefficients for the additional terms.

Table X shows the constants extracted from a fit of the transitions listed in Table IX to equation (8) above plus the two additional terms. Note that two of the first order anharmonicity constants, x_{RR} and x_{sR} , are reversed in sign from the expected for diatomic-like stretching motions, which describe vibrational energy spacings that increase with vibrational quantum. This is not unreasonable for the bending and rocking modes and these motions do not correlate to a dissociation coordinate. Therefore the corresponding potential need not look like a typical diatomic curve. The diagonal anharmonicity, x_{ss} , for the complex stretching motion is of the expected sign (positive) for a motion which correlates to the dissociation of the electrostatic bond. The magnitudes of x_{ss} and ω_s may be used to estimate the binding energy of the complex from the hackneyed relation derived for a Morse potentialⁱⁱ.

ⁱⁱThe constants D_0 , ω_i and x_{ii} could be replaced with the equilibrium values, but the accuracy of the prediction does not warrant the effort.

$$D_0 \approx \frac{\omega_i^2}{4 x_{ii}} \quad (9)$$

This relation places the diabatic dissociation energy of the excited ($\tilde{A}'$) state of the complex at 4400 cm^{-1} (0.55 eV).

Figure 46 shows a 'closeup' of the electronic origin of the $\tilde{A}'$ - $\tilde{X}$ system and a simulation of the rotational contour. In CoAr^+ , the A' -X transition is an $\Omega' = 4 - \Omega'' = 3$ transition, and if the CoOCO^+ molecule is linear, the same is expected to be true here. Although by no means definitive, the agreement between observed and calculated contours is gratifying, suggesting that the complex is indeed linear in its ground state. A rotational temperature of 7 K and linewidth of 0.2 cm^{-1} is assumed in the simulation. The value of the lower-state rotational constant of 0.0537 cm^{-1} allows the complex geometry to be determined if the CO_2 fragment geometry has not changed much upon complexation. Under this assumption, the distance between the Co^+ ion and the center of mass of the CO_2 (the C atom) is 3.30 Å in the ground vibronic state. The vibrationless level of the $\tilde{A}'$ excited state has a slightly greater Co^+ -C distance of 3.47 Å, as expected. This analysis indicates that the distance between the metal ion and the oxygen atom 'in contact' is 2.14 Å and 2.31 Å in ground and excited states respectively.

The $\tilde{A}'$ - $\tilde{X}$ electronic transition probed by photofragmentation is derived from a parity forbidden (in the isolated metal ion) transition which involves an electronic configuration change from $3d^8$ in the ground state to $3d^74s$ in the excited state. Thus, the

excited state is expected to have increased the repulsion between the metal and the ligand with respect to the ground state and thus a change in the equilibrium geometry is expected between these two states. This results in progressions in the $M^+ \leftrightarrow L$ stretching mode, ν_s . Still, no observation of activity in the CO_2 asymmetric stretching mode can be confirmed. The CO_2 moiety seems 'rigid' with respect to the soft complex modes. Note, however, that the conceptual separation of interfragment and interfragment forces and vibrations is intrinsic to the definition of a 'cluster'.

Only the diagonal stretching mode anharmonicity, x_{ss} , is of the 'normal' sense, i.e. vibrational levels becoming closer as the energy increases. The stretching mode frequency and anharmonicity correspond to the motion of complex dissociation and have been used (above) to estimate the excited state binding energy of the ion, 4400 cm^{-1} . This value is in the ballpark of the binding of other electrostatic complexes of Co^+ but is expected to represent a lower limit to the true binding energy. This is because of the improper asymptotic behavior of the Morse potential applied to a dissociating ion. However, if this excited state binding energy is correct, this places the $CoOCO^+ \rightarrow Co^+ d^7s (^3F_4) + CO_2 ^1\Sigma_g^+$ limit at $12375 + 4400 = 16775\text{ cm}^{-1}$. Subtraction of the promotion energy¹² of the $Co^+ d^7s (^3F_4)$ state above the ground $Co^+ d^8 (^3F_4)$ state yields an estimate of the bond strength in the ground state of the complex of 6960 cm^{-1} . This too is expected to be a lower limit. This value may be compared with a binding energy of 4110 cm^{-1} in $CoAr^+$ and 5400 cm^{-1} in $CoKr^+$.

The rotational structure of the vibronic bands in the $\tilde{A}'-\tilde{X}$ system has been successfully fit using a linear equilibrium geometry for the complex, but because of the

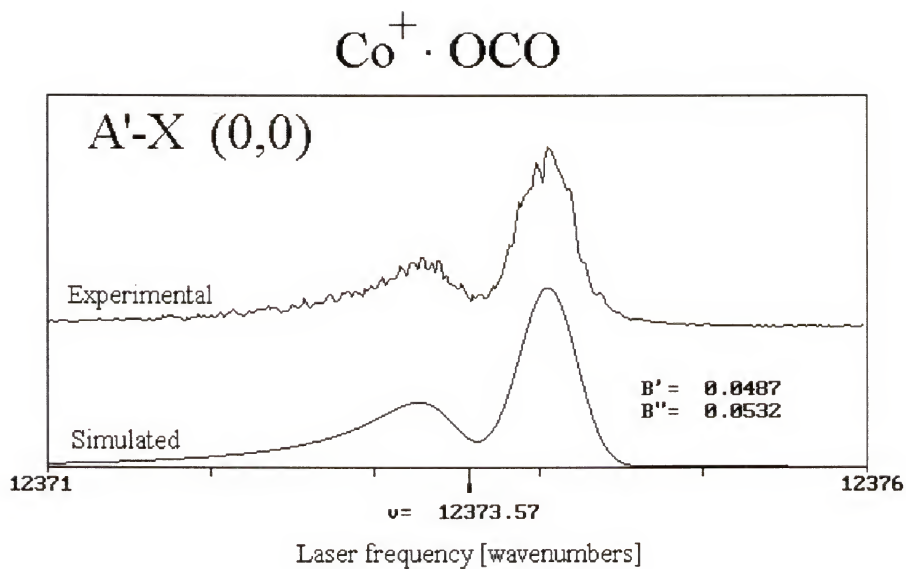


Figure 46. $\text{CoCO}_2^+ \tilde{\text{A}}' - \tilde{\text{X}} (0,0)$ Transition Rotational Detail.

The figure shows a closeup of the origin of the $\tilde{\text{A}}' - \tilde{\text{X}}$ transition (upper curve) and a simulation of the rotational contour, assuming a linear ground state geometry with $\Omega''=3$. The rotational constants indicates that the metal-carbon separation is 3.30 Å in the vibronic ground state of the molecule.

rather incomplete resolution of the rotational structure, the geometry of this molecule has not been determined conclusively. The rotational constants and electronic orbital angular momentum in both ground and excited states are entirely consistent with that of the analogous transition in CoAr^+ , where more complete rotational resolution was obtained. If this analysis is correct, the Co^+ -O distance in the ground state of Co^+OCO at 2.14 Å is shorter than the Co^+ -Ar distance in CoAr^+ (2.385 Å) by 10%.

The rocking motion is quite anharmonic and exhibits a potential that is 'steeper' than parabolic. This indicates that the rocking potential has significant contributions from terms of the type $(1-\cos\theta)^n$, where $n>1$. The polarizability of the CO_2 is of course anisotropic and greatest along the double bonds, which contributes to the stiffness of the rocking motion.

The stretch and the rock vibrational frequencies determined for this ion are listed in **Table X**. These may be compared with those of a similar ion complex²⁵, V^+OCO . In this ion, the stretching frequency in the d^3 s excited state was found to be 196 cm^{-1} , quite similar to the 188 cm^{-1} found in this complex. However, the rocking frequency of V^+OCO is 105 cm^{-1} , much greater than the 65 cm^{-1} found here. Arguments have been presented for the geometry of the vanadium electrostatic complex being non-linear (C_s symmetry), which may explain this difference.

Table XI gives the assigned transitions in **Figure 45** and transitions not included in $\tilde{A}'$ from **Figure 44**. The splitting in the blue portion of the CoCO_2^+ spectrum has not been fully analyzed, however, there are at least two additional states and possibly a third perturbing the ones labeled $\tilde{B}-\tilde{X}$ and $\tilde{C}-\tilde{X}$. The spectroscopic constants, which have been

Table XI. CoOCO^+ Band Origins for $\tilde{a}-\tilde{X}$, $\tilde{B}'-\tilde{X}$, $\tilde{B}-\tilde{X}$, $\tilde{C}-\tilde{X}$ and $\tilde{D}-\tilde{X}$ transitions.

v	$\tilde{a}-\tilde{X}$	$\tilde{B}'-\tilde{X}$	$\tilde{B}-\tilde{X}$	$\tilde{C}-\tilde{X}$	$\tilde{D}-\tilde{X}$
0	12301.10	13752.00	15156.80	15178.20	15009.50
1		13936.40	15366.80	15379.30	15247.90
2		14124.00	15565.00	15572.30	15473.70
3		14311.00	15764.50	15773.50	15682.90
4		14493.10	15954.20	15957.80	15886.40
5		14669.80	16142.50		16082.50
6		14839.10	16326.40		16276.40
7			16506.50		
8			16682.90		
9			16856.30		
10					

Table XII. Properties, in wavenumbers, of the observed states of CoCO_2^+ .

State	T_{e0}^i	ω_e	$\omega_e x_e$	$\omega_e y_e$
a	12200 $\pm$ 50			
B'	13660	181.0	-2.83	-0.428
B	14883	258.1	10.26	0.544
C	15051	213.1	3.03	0.627
D	15081	192.9	-3.79	-0.746

ⁱ T_{e0} is the electronic term energy relative to the zero point level of the X state

extracted for the lines listed in Table XI, are given in Table XII. The stretching

frequencies of the $\tilde{B}'$ state are similar to that of the $\tilde{A}'$ state and one is possibly part of an

asymmetric stretch progression which is built upon it. Until the isotopic analysis, in particular for studies with $^{16}\text{OC}^{18}\text{O}$, can be done this remains unknown.

Nickel Carbon Dioxide Cation

The behavior of charged particles in liquids is dominated by electrostatics, which, because of their long range, includes the participation of many neutral solvents for each charged solute. To model liquids, it is important to determine the magnitude of the electrostatic interaction of an ion to a single solvent 'ligand', in the absence of a corpuscular dielectric medium of the bulk liquid.

The binding energy of a transition-metal ion, Fe^+ , to CO_2 has been the subject of a recent ICR mass-spectrometric investigation²⁶. The electrostatic complex, $\text{Fe}^+\cdot\text{CO}_2$, was formed by a clever ion-molecule reaction in the gas phase and subjected to collisions during storage in an ion trap. The binding energy of the complex was then bracketed by the behavior of ligand exchange reactions²⁷ with neutral collision partners whose binding energies with Fe^+ have been previously measured or calculated. Ligand exchange in $\text{Fe}^+\cdot\text{CO}_2$ was found to occur with Xe but not Ar, placing the dissociation energy of the complex at 8 ± 2 kcal/mol (2800 ± 700 cm⁻¹).

A study of the binding energy of a similar compound, $\text{Ni}^+\cdot\text{CO}_2$, is performed here in quite a different manner. The ion cluster is formed by the supersonic expansion of a laser-driven plasma, and isolated in the gas phase with a minimum of internal energy. Narrow-band visible light is used to induce electronic excitation in the ion, and the resulting fragmentation (if any) is monitored by tandem mass selection. The photon

energy employed is sufficient to access electronic states high above the adiabatic binding energy of the complex, but which are relatively long-lived with respect to dissociation due to weak coupling to the continuum of the ground state. The metastable excited states of the complex show sharp optical transitions from the ground state and the interpretation of these spectral features yields a wealth of information about the excited states. This type of data has been analyzed for a similar ion-CO₂ complex, Co⁺·OCO which was discussed above. In this case, however, the photophysics of the predissociation of the Ni⁺·CO₂ yields a direct measure of the ground state binding energy of the molecule.

Figure 47 shows the relative photofragmentation yield $\text{Ni}^+\cdot\text{OCO} + h\nu \rightarrow \text{Ni}^+ + \text{OCO}$ as a function of laser frequency in the region of 16300 cm⁻¹ to 18100 cm⁻¹. This figure shows the spectrum of only one of the isotopically selected variants of the molecule, the most abundant: ⁵⁸Ni⁺·OCO. Simultaneous observation of more than one isotopomer is a distinct advantage in the analysis of an optical spectrum. Moreover, the spectra obtained here do not suffer from the congestion normally associated with mass-unresolved samples.

The electronic transition probed by photofragmentation in this complex is derived from a parity forbidden 3d⁸4s – 3d⁹ transition in the isolated metal ion. The metal ion electronic configuration in the upper state of the transition has a larger repulsive interaction with the 'ligand' in the complex which results in an increase in ion-ligand equilibrium separation and long progression in the complex M⁺↔(OCO) stretching mode upon absorption. The Ni⁺ 3d⁸4s electronic configuration has two low-lying electronic terms, a ²F_J and a ⁴F_J manifold. The molecular states derived from the doublet term will

$\text{Ni}^+ \cdot \text{OCO}$ Resonant Photodissociation

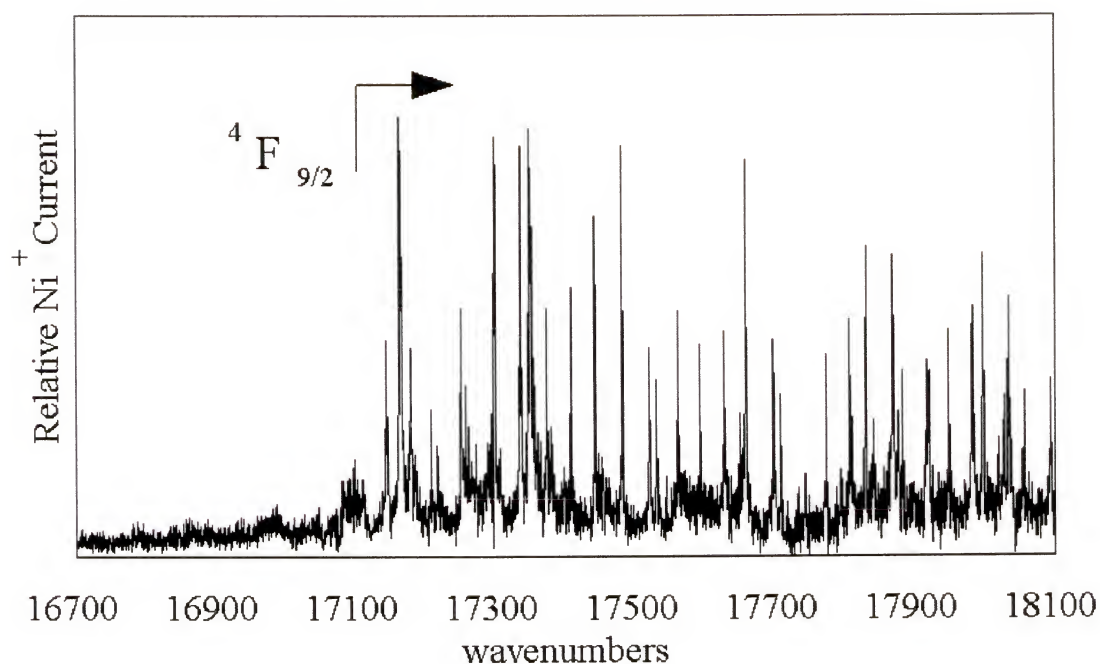


Figure 47. $\text{Ni} \cdot \text{CO}_2^+$ Photodissociation Spectrum.

The figure shows a resonant photodissociation spectrum of the $^{58}\text{Ni}^+ \cdot \text{OCO}$ complex with yellow light. The vertical axis is relative Ni^+ photocurrent and the horizontal is dissociation laser frequency in wavenumbers. The sharp feature evident in the blue part of the spectrum extends to higher frequency but no resonant structure is observed to lower frequency than this figure. The onset of resonant dissociation occurs at the energetic threshold for production of $\text{Ni}^+(^4F_{9/2}) + \text{CO}_2(^1\Sigma_g^+)$, which is indicated in the figure. This places the adiabatic binding energy of the $\text{Ni}^+ \cdot \text{OCO}$ complex at 1.08 ± 0.01 eV.

exhibit a spin-allowed electric-dipole transition from the ground state of the ion which is derived from the ^2D_J ground state atomic term. This doublet-doublet transition has been observed in NiAr^+ discussed in the previous chapter.

The congested sharp line portion of the spectrum displayed in **Figure 47** corresponds to Hunds case (a) allowed transitions whose upper states correspond to the excited $\text{Ni}^+(^2F_J) + \text{CO}_2(^1\Sigma_g^+)$ limit. These electronic transitions, it should be noted, are detected by dissociation into a lower limit. Several electronic transitions are evident in this portion of the spectrum along with associated excited-state vibrational progressions. The analysis of these band systems is underway. An abrupt cutoff of the sharp dissociation feature occurs at 17100 cm^{-1} below which only non-resonant photodissociation is observed. Both the vibrational structure of the resonant features and the $^{58}\text{Ni}^+\cdot\text{OCO}$ - $^{60}\text{Ni}^+\cdot\text{OCO}$ isotope shift (ca. 2.4 cm^{-1} in the region of the cutoff, as shown in **Figure 48**) unambiguously rule out the region around 17100 cm^{-1} as an electronic origin. This cutoff does not correspond to a break in the ions absorption but rather to a change in the dissociation yield. This change is at the threshold for dissociation into the next lower dissociation limit, that of $\text{Ni}^+(^4F_J) + \text{CO}_2(^1\Sigma_g^+)$.

The energy of the lowest state arising from the excited d^8 s configuration¹² is the $^4F_{9/2}$ state of Ni^+ and is 8394.1 cm^{-1} above the ground $3d^9(^2D_{5/2})$ level of the atomic ion. If the threshold for this limit is placed at $17100 \pm 100\text{ cm}^{-1}$ in the complex, then adiabatic binding energy of the molecule is $8700 \pm 100\text{ cm}^{-1}$ ($1.08 \pm 0.01\text{ eV}$).

The binding energy of this complex is roughly twice that of NiAr^+ $4572 \pm 5\text{ cm}^{-1}$ (or 0.567 eV). The polarizability²³ of Ar is $1.66\text{ \AA}^3$ compared to that of CO_2 of $4.03\text{ \AA}^3$

$\text{Ni}^+ \cdot \text{OCO}$ Resonant Photodissociation

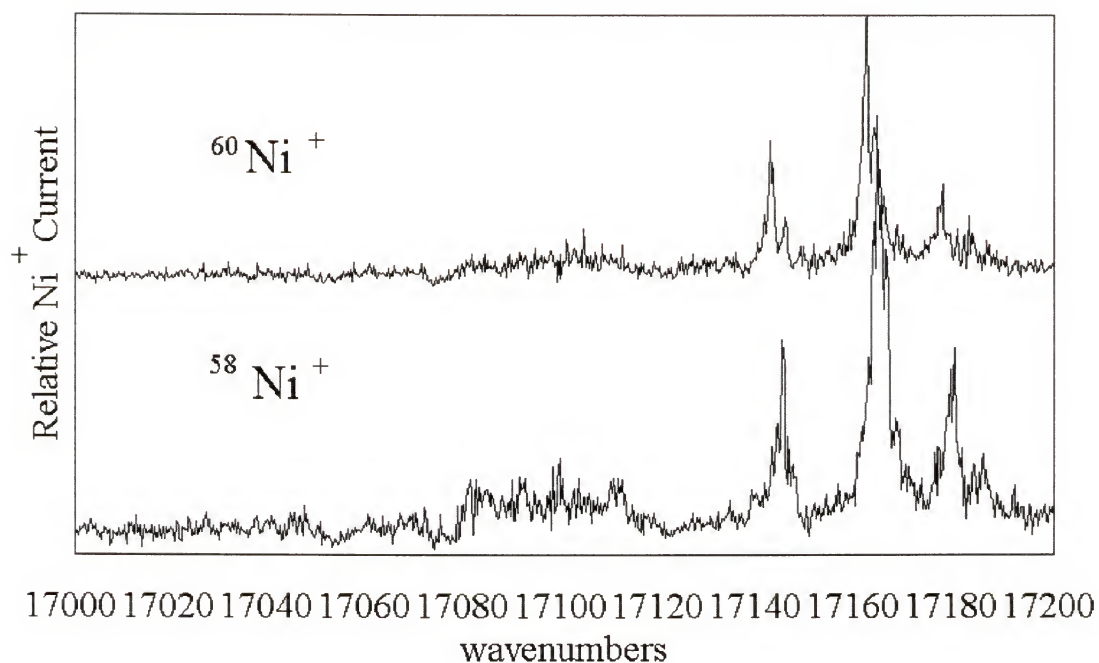


Figure 48. $\text{Ni} \cdot \text{CO}_2^+$ Photodissociation Spectrum.

The figure shows isotope shift in the dissociation spectrum of the $^{58}\text{Ni}^+ \cdot \text{OCO}$ and $^{60}\text{Ni}^+ \cdot \text{OCO}$. The vertical axis is relative Ni^+ photocurrent and the horizontal is dissociation laser frequency in wavenumbers. The isotope shift in this region is about 2.4 cm^{-1} .

and $1.93\text{\AA}^3$, parallel and perpendicular to the C_∞ axis respectively. If the binding in the complex is simply charge-(induced-dipole) the binding energy should scale like the polarizability of the neutral partner but be inversely proportional to the fourth power of the center-to-center separation of the interacting fragments. If the $\text{Ni}^+\cdot\text{OCO}$ complex is T-shaped (C_{2v}), and the Ni^+ -C distance is roughly that of Ni^+ -Ar, the relative binding of CO_2 versus Ar should be in the ratio of $1.93/1.66=1.16$. If the Ni^+OCO complex is linear then the (closer) Ni^+ -O distance should be similar to that of Ni^+ -Ar and about $2.37\text{\AA}$ (from *ab initio* theory⁹). If the CO_2 is undistorted upon complexation, then the Ni - C distance is $3.54\text{\AA}$, making the relative binding of $\text{CO}_2/\text{Ar} = (4.03/1.66)(2.37/3.54)^4 = 0.49$. Clearly, the charge-(induced-dipole) model for complexes of CO_2 is inadequate to describe the binding energy

The binding in $\text{Ni}^+\cdot\text{OCO}$ is greater than that found for $\text{Fe}^+\cdot\text{OCO}$ or $\text{Co}^+\cdot\text{OCO}$ (6960 cm^{-1}). A d-orbital contraction is expected to at least partially explain a reduced repulsion and greater binding in the late transition-metal electrostatic complexes. Precise determination of the properties of complexes like these is leading to a greater understanding of the variation of binding with respect to transition-metals and the contribution to the binding by forces more subtle than charge-(induced-dipole).

Cobalt Nitrogen Cation

The electrostatic complex of Co^+ with a single N_2 molecule has been prepared and studied by optical excitation of the metal ion. Vibrational structure of such electronic transitions shows excited state progressions of the complex modes. A single far-red

transition shows little geometry change upon excitation and displays the rotational contour of a non-linear complex. Yellow transitions show vibrational structure indicative of a gross geometry change with progressions in both stretching and rocking modes. This suggests that CoN_2^+ possesses a 'T'-shaped ground state and both linear and non-linear excited states. A particular linear upper state, the $\tilde{\text{B}}$ state, is characterized vibrationally with a typical metal-ligand stretching frequency (140 cm^{-1}) but a rather flaccid rocking frequency (14 cm^{-1}). The geometry change upon $3d^74s \rightarrow 3d^8$ excitation²⁸ of the Co^+ ion in this complex is discussed in terms of a simple model potential which includes both electrostatic and inductive components.

To understand the behavior of molecules in intimate contact with each other, it is important to differentiate among the attractive forces between non-bonded molecules. These forces have been categorized into three types: electrostatic, inductive, and dispersive forces. The dispersive attraction between molecules is ubiquitous and arises because of the correlated fluctuations of the electron density in each entity. The electrostatic forces are so called because they arise from Coulombic interaction between the static and unperturbed electron distributions of the individual molecules. The inductive forces are Coulombic interactions between the static charge distribution of one species and the distortion induced in the electron distribution of the other species. It is also useful to further subdivide the inductive and electrostatic forces in terms of the angular symmetry of the static or induced charge distributions of the interacting molecules (multipole expansion)²⁹.

The electrostatic interaction of an electric monopole (charge) and a polar (electric-dipole) neutral molecule is the dominant long-range solute-solvent force in electrolytic solution. If the solute has no permanent dipole moment; i.e., is non-polar, then the interaction of the charge with the next higher moment of the neutral, the quadrupole, is dominant. The $\text{Co}^+\cdot\text{N}_2$ complex exemplifies this charge-(permanent-quadrupole) force.

Even though a long-range electrostatic interaction exists between the metal ion and the N_2 ligand in this complex, inductive forces cannot be ignored. The charge-(induced-dipole) force in this complex is significant and is only slightly shorter ranged than the electrostatic charge-quadrupole; the former scales like $1/r^4$ and the latter like $1/r^3$. These inductively-bound ion complexes have been studied before²⁰ and are ideally modeled by ion-(rare-gas) complexes. In the context defined above, these have no purely electrostatic interaction. The inductive forces in $\text{Co}^+\cdot\text{N}_2$ are more complicated than in rare-gas complexes, however, since this force depends on the alignment of the N_2 fragment with respect to the position of the ion and anisotropy of the N_2 polarizability. The magnitude of the inductive interaction between ion and neutral is in fact larger than the electrostatic interaction at the equilibrium geometry of CoN_2^+ .

The detailed experimental study of isolated complexes which exhibit only simple electrostatic and inductive forces is an appropriate theater for the quantification of the interactions that dominate in the condensed phase. In the case of $\text{Co}^+\cdot\text{N}_2$, the balance of electrostatic and inductive interactions causes different states of the ion to exhibit different

equilibrium geometries. The optical spectrum of $\text{Co}^+\cdot\text{N}_2$ helps reveal the details of these forces.

The optical spectrum of isolated, gas-phase, CoN_2^+ is obtained by photodissociation excitation spectroscopy¹⁸, i.e. detection of fragment photocurrent arising from the one-photon dissociation of mass-selected parent ions. Spectra are obtained from continuous frequency scans of a visible dye-laser (ca. 10 mJ/cm²·pulse; 7 ns pulse) inducing dissociation only on resonance with an electronic absorption. Rotational analysis of spectra obtained from other cluster cations produced under similar conditions show that the nascent ions are generated internally cool ($T_{\text{ROT}} < 10$ K). Transition frequencies are calibrated against Ne optogalvanic lines and are quoted at a beam energy of 1.45 kV. The transition frequencies observed are Doppler shifted by +3.0 cm⁻¹ with respect to the true rest frequencies of the molecule. Naturally, this shift is corrected for in the determination of molecular constants.

Figure 49 shows the resonant photofragmentation spectrum of CoN_2^+ in the frequency range of 12800 to 18300 cm⁻¹. The only observed photofragmentation pathway at this photon energy is $\text{CoN}_2^+ \rightarrow \text{Co}^+ + (\text{N}_2)$, the reverse of the process for complex formation in the ion source. This relative fragmentation is plotted versus laser frequency to give the spectrum in Figure 49.

The features observed here are similar to absorptions in the CoAr^+ , CoKr^+ , CoXe^+ , and $\text{Co}\bullet\text{OCO}^+$ ions, investigated in our laboratory and discussed in previous sections. The resonant absorptions of this ion, like the ions just mentioned, result from

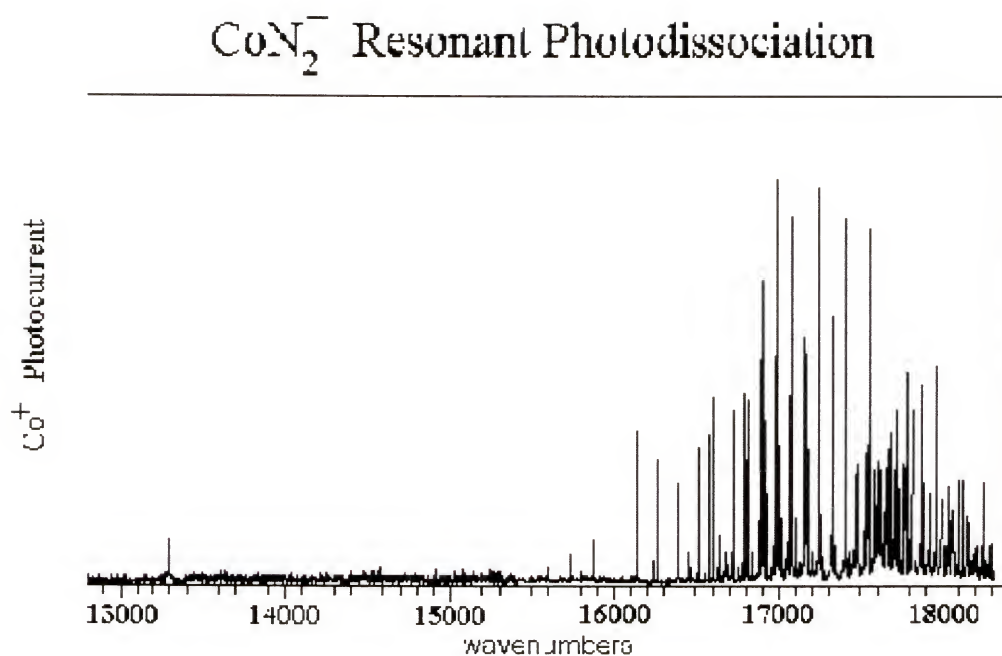


Figure 49. Photodissociation Spectrum of CoN_2^+ .

The figure shows a portion of the resonant photodissociation spectrum of CoN_2^+ in the region of 12800 cm^{-1} to 18300 cm^{-1} . The horizontal axis is the dissociation laser frequency and the vertical axis is relative Co^+ photocurrent resulting from the fragmentation of mass selected CoN_2^+ .

Table XIII. CoN_2^+ band origins for the $\tilde{\text{B}}-\tilde{\text{X}}$ electronic transitions.

Observed	Obs-Calc	ν_{R}	ν_{S}	Observed	Obs-Calc	ν_{R}	ν_{S}
15594.1	-2.2	4	0	16456.2	-0.7	2	7
15735.0	0.3	4	1	16579.6	1.7	2	8
15872.0	1.4	4	2	16697.6	1.3	2	9
16006.0	2.1	4	3	16811.5	-0.8	2	10
16136.2	1.4	4	4	16924.8	-1.0	2	11
16263.1	-0.1	4	5	17038.0	1.2	2	12
16387.2	-2.0	4	6	16554.4	-2.8	1	8
16510.2	-2.4	4	7	16676.6	1.0	1	9
16632.5	-1.0	4	8	16793.2	1.6	1	10
16754.3	2.4	4	9	16904.0	-1.0	1	11
16232.7	-0.3	3	5	17015.3	-0.7	1	12
16360.2	1.3	3	6	16776.2	0.6	0	10
16483.2	0.9	3	7	16888.4	-0.6	0	11
16602.5	-0.8	3	8	17000.7	0.7	0	12
16720.1	-1.7	3	9				
16836.7	-1.0	3	10				
16952.5	1.3	3	11				

more than one electronic transition and consequently more than a single set of vibrational transitions.

Like all the electrostatic ion complexes listed above, CoN_2^+ has two distinct classes of low-lying excited electronic states, those derived from the $3d^74s$ electronic configuration of the Co^+ ion and those derived from the $3d^8$ configuration. The ground state is derived from the latter manifold and possesses a geometry indicative of a relatively small Co^+ ionic radius. An excited state corresponding to the same electronic configuration as the ground state, as exemplified by diagonal Franck-Condon factors of the electronic transition from the vibrationless ground state, has been found in the absorption of CoAr^+ at 12550 cm^{-1} , CoXe^+ at 12570 cm^{-1} , and $\text{Co}\cdot\text{OCO}^+$ at 12300 cm^{-1} . The corresponding electronic transition in the $\text{Co}^+\cdot\text{N}_2$ complex can be seen as a weak feature in **Figure 49** at 13297 cm^{-1} and is assigned the label $\tilde{a}-\tilde{X}$. Only the origin of this system is seen; no hot bands or off-diagonal vibrational transitions are observed.

The complete rotational structure of the $\tilde{a}-\tilde{X}$ origin band is not resolvable in our present apparatus. The rotational contour of the band has been simulated using resolution and temperature parameters that have been successfully applied to rotational fits of CoOCO^+ , and CoAr^+ and ZrAr^+ spectra taken in the same machine. These fits are not able to determine the precise geometry of the molecule. However, the electronic states involved in the $\tilde{a}-\tilde{X}$ system do not have a linear equilibrium geometry. If the ground state were linear, it would be expected to have $\Omega''=3$, in analogy to CoAr^+ and CoOCO^+ , and this would result in a distinctive band shape in an electronic transition to another linear state. This bandshape is not observed.

Table XIV. $\text{CoN}_2^+ \tilde{\text{B}}$ State Spectroscopic Parameters in cm^{-1} .

Parameters	Value in cm^{-1}
T_{00}	15500.00
ω_{S}	139.60
ω_{R}	13.60
x_{SS}	-1.24
x_{RR}	2.37

To the blue of the $\tilde{\text{a}}\text{-}\tilde{\text{X}}$ system, several electronic transitions appear with apparently greater oscillator strength and drastically different vibrational structure. These transitions have upper states which correspond to $3\text{d}^74\text{s Co}^+$, and thus a significant change in equilibrium metal-ligand separation upon excitation from the ground state.

Figure 50 shows vibronic bands of the $\tilde{\text{B}}\text{-}\tilde{\text{X}}$ electronic transition in the cobalt-nitrogen ion complex. These are all cold-band transitions and represent activity (progressions) in two upper-state normal-modes. Table XIII lists the transition frequencies of the portion of the bands in Figure 50 that have been assigned to progressions in the complex stretching and rocking motions on a single upper electronic surface. The assigned vibrational numbering has yet to be confirmed by isotope substitution analysis. The vibrational structure evident in this band system indicates an overall equilibrium geometry change between the vibrationless ground state and the upper electronic state.

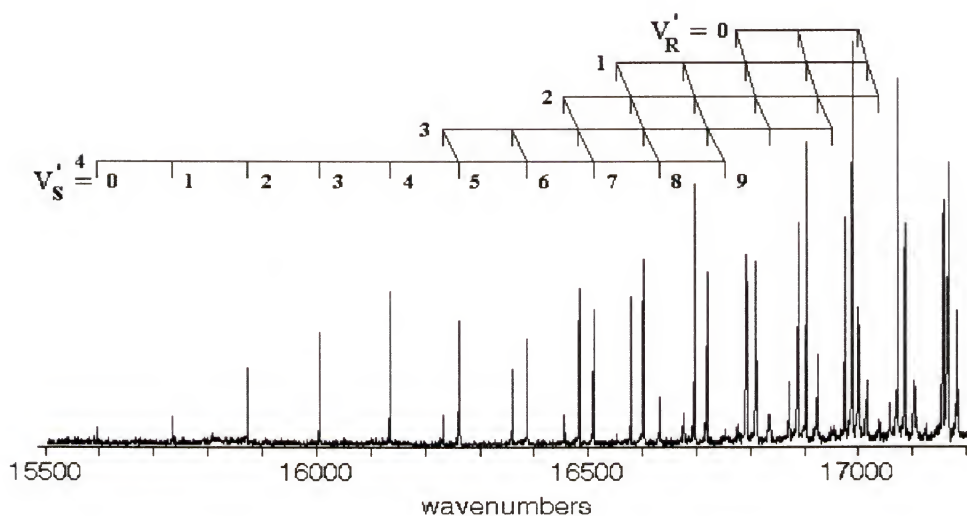
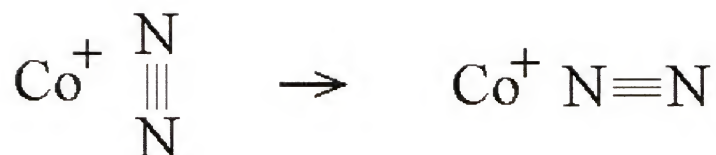


Figure 50. $\text{Co} \cdot \text{N}_2^+$ Vibrational Progression.

A closeup of the $\text{Co} \cdot \text{N}_2^+ \tilde{\text{B}}-\tilde{\text{X}}$ transition including upper state vibrational quantum number assignments. This spectrum is unlike that of the $\text{Co} \cdot \text{CO}_2^+$; the origin ($v_s=0$, $v_r=0$) is not seen in the time scale of our experiment, indicating that the geometry change from ground to excited state is significant.

Fits of the 31 band positions of the $\tilde{B}-\tilde{X}$ system to functional forms of the standard type³ have been performed and the deviation between observed and calculated line positions has been examined. The goal is to find just the parameters that are determined by the subset of energy levels observed in the spectrum. The simplest form that successfully fits the experimental band positions contains only two anharmonicity parameters, the diagonal first-order stretch and rock anharmonicities and has the form:

$$v(B(v_S, v_R) - X(0, 0)) = T_{00} + \omega_S v_S + \omega_R v_R + x_{SS} v_S^2 + x_{RR} v_R^2 \quad (10)$$

where v_S and v_R are the stretch and rock upper state vibrational quantum numbers, T_{00} is the electronic origin, ω_S and ω_R are the stretch and rock harmonic frequencies, x_{SS} , and x_{RR} are the first-order anharmonicity constants. Note that no cross anharmonicity term, x_{SR} , is necessary to fit the observed data. The RMS deviation of the fit to the above equation is 1.4 wavenumbers, slightly above estimated experimental error in the band positions.

Table XIV shows the constants extracted from a fit of the transitions observed in **Table XIII** to the equation above. Note that the first-order anharmonicity constant for the rocking motion, x_{RR} , is reversed in sense (sign) from that expected for diatomic-like stretching motions, i.e. they describe vibrational energy spacings that increase with vibrational quantum. This is not unreasonable for the bending and rocking modes, since these motions do not correlate to a dissociation coordinate and the corresponding potential need not look like a typical diatomic curve. The diagonal anharmonicity, x_{SS} , for the complex stretching motion is of the expected sign (negative) for a motion which correlates to the dissociation of the electrostatic bond. The magnitude of the binding

energy in the $\tilde{B}$ state of the complex may be estimated³ assuming a linear Birge-Sponer relation (or alternatively a Morse potential function for the upper state) as $D_0 \approx -\omega_{ss}^2/4x_{ss} = 3900 \text{ cm}^{-1}$ (0.49 eV). The diabatic limit for the dissociation of this state is then $T_{00} + D_0 \approx 19430 \text{ cm}^{-1}$.

Figure 51 shows another visualization of the $\tilde{B}$ - $\tilde{X}$ spectrum in which the data has been overlapped to compare systematically transitions to successively higher stretching quanta after excitation. Figure 51 is merely the data of Figure 50 'overlapped' upon itself at the approximate upper state vibrational first difference, ΔG . This representation allows for an examination of the intensity distribution of the vibronic bands and thus information on the Franck-Condon factors associated with the electronic transition.

Figure 51 shows the transitions with the same value of upper state rocking quantum number, v_R , grouped in vertical stripes with the position within the stripe indicating the stretching quantum number, v_S , in the upper state. For transitions to states of low v_S , only high v_R transitions have significant intensity. As the upper state stretching quantum, v_S , increases, the intensity pattern shifts to lower v_R , indicating a better overlap of the vibrational wavefunction with small rocking quanta at larger interparticle separation. The projection of the ground state vibrational wavefunction upon electronic excitation is to the repulsive wall of the upper state. That portion of the wavefunction high on the wall has better overlap with excited state wavefunctions of low v_R , due to the difference in the geometries of the ground and excited states.

CoN_2^+ "Overlapped" Spectrum

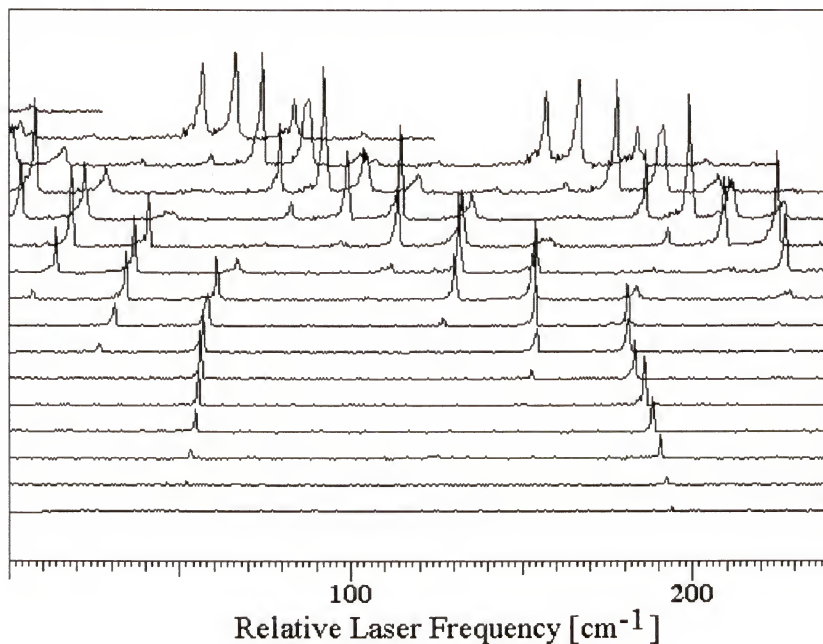


Figure 51. $\text{Co}\cdot\text{N}_2^+$ Overlapped Spectrum.

The figure shows the same spectrum as seen in Figure 50 'overlapped' with itself at a frequency displacement corresponding to a quanta of stretching motion. This allows the intensity distribution of the Stretch+Rock transitions in the system to be visualized easily. The intensity distribution is indicative of a geometry change upon electronic excitation.

If the CoN_2^+ cluster is rigid enough for a separation of rotational and vibrational motion, there are $3N-6=3$ normal modes of vibration. The vibrational modes that correspond to complexation are the $\text{Co}^+ \rightarrow (\text{N}\equiv\text{N})$ stretch and $\text{Co}^+ - \uparrow(\text{N}\equiv\text{N})\downarrow$ rock. These motions appear to be separable from each other and the remaining normal mode, the intrinsic $\text{N}\rightarrow\text{N}$ stretch.

The $\tilde{\text{B}}-\tilde{\text{X}}$ electronic transition probed by photofragmentation is derived from a parity forbidden (in the isolated metal ion) transition which involves an electronic configuration change from $3d^8$ in the ground state to $3d^74s$ in the excited state. Thus, the excited state is expected to have an increased repulsion between the metal and the ligand with respect to the ground state and therefore a change in average equilibrium separation between ion and neutral is expected between these two states. This results in progressions in the $\text{M}^+ \rightarrow \text{L}$ stretching mode. The stretching-mode anharmonicity, x_{SS} , is of the 'normal' sense, i.e. vibrational levels becoming closer as the energy increases. The stretching mode frequency and anharmonicity correspond to the motion of complex dissociation and have been used (above) to estimate the excited state binding energy of the ion, 3900 cm^{-1} . This value is in the ballpark of the binding of other electrostatic complexes of Co^+ but is expected to represent a lower limit to the true binding energy.

$\text{Co}\cdot\text{N}_2^+$ Model Potential

Is it reasonable that the CoN_2^+ complex undergo such a drastic change in geometry upon electronic excitation, given that both the upper and lower states are bound by the same electrostatic and inductive forces? In order to address this question, estimates of the forces of interaction between atomic ion and neutral ligand may be made.

The long-range attractive forces have contributions from the interactions between the permanent multipole moments of the charge distributions of the fragments. The leading term in this electrostatic interaction is the charge - quadrupole. If we take the cobalt cation to be the position of a formal +1e charge and the quadrupole moment of the N₂ in the complex equal to that of the free molecule, the electrostatic potential in the complex is

$$V_{\text{electrostatic}}(R, \theta) = \frac{qQ}{2R^3} (3\cos^2\theta - 1) \quad (11)$$

where R is the distance between the Co⁺ and the center of mass of the N₂ and θ is the angle between the line of centers and the N≡N bond. A literature value²³ for the N₂ quadrupole is -1.5×10^{-26} esu·cm². This quadrupole is about three times smaller than that of CO₂ and of the same sign, indicating excess negative charge at the ends of the molecule relative to that of the middle. This term in the potential favors a linear geometry for the complex at constant R and is in fact repulsive for a 'T'-shaped molecule.

The leading term in the inductive part of the attraction is the charge-(induced-dipole) and depends on the details of the dipole polarizability tensor of the neutral. Since the N₂ is axially symmetric, only the polarizability along and perpendicular to the bond axis are needed to describe this tensor. The inductive potential, then, also has a second-Legendre-moment dependence in the angle θ ,

$$V_{\text{inductive}}(R, \theta) = \frac{q^2}{6R^4} [(\alpha_{\parallel} + 2\alpha_{\perp}) + (\alpha_{\parallel} - \alpha_{\perp})(3\cos^2\theta - 1)] \quad (12)$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the parallel and perpendicular components of the dipole polarizability and have values²³ of 2.22×10^{-24} and $1.54 \times 10^{-24} \text{ cm}^2$ respectively. Although the qualitative results of this presentation are unaffected by the exact choice of these polarizability values, experience in modeling ion-(rare-gas) complexes leads us to choose slightly larger values for the polarizabilities than that obtained from bulk measures. The values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ used in this model are 2.89×10^{-24} and $2.00 \times 10^{-24} \text{ cm}^2$, a factor of 1.3 larger than in reference²³. The charge induced dipole force in this complex is attractive for all angles θ and also favors a linear geometry at all constant R .

The repulsive force between ion and ligand 'balances' the long ranged attractive forces at the equilibrium geometry of any particular electronic state. The repulsive force is a function of the electronic configuration of the Co^+ ion and thus the ion 'size'. The form of this potential is not simple, but is nonetheless much 'steeper' and shorter-ranged than the attractive forces described above. A guess at the repulsive potential might look like a Born-Mayer form:

$$\mathbf{V}_{\text{repulsive}}(R, \theta) = a_0 e^{-\rho_0 R} + a_2(3\cos^2\theta - 1)e^{\rho_2 R} \quad (13)$$

This functional form has an abundance of unknown parameters but suggests that the repulsion transforms (approximately) as a monopole and a quadrupole. If the repulsion is considered a 'hard wall' then the Co^+ may be thought of as butting up against the anisotropic shape of the N_2 with a distance of closest approach given by:

$$R_{\text{rep}}(\theta) = [R_{\text{avg}} + \frac{(R_{\parallel} - R_{\perp})}{3}(3\cos^2\theta - 1)] \quad (14)$$

where $R_{\text{avg}} = (R_{\parallel} + 2R_{\perp})/3$ is the average ion-ligand separation. The magnitude of the anisotropy of the N_2 molecule may be guessed under the assumption that the length of the molecule^{2, 3, 4, 5}, $R_{\parallel}$, is longer than its width, $R_{\perp}$, by the bond length, i.e., $R_{\parallel} - R_{\perp} = 0.55 \times 10^{-8}$ cm. The potential at the optimal R , $V_{\text{min}}(\theta)$, is approximately the sum of the leading attractive terms evaluated at the repulsive wall:

$$V_{\text{min}}(\theta) = V_{\text{electrostatic}}(R_{\text{rep}}, \theta) + V_{\text{inductive}}(R_{\text{rep}}, \theta) \quad (15)$$

The electrostatic term still always favors linearity but now the inductive term favors a geometry with $\theta=90^\circ$. It is the balance of these two forces that determines the equilibrium geometry of any state of the molecular ion. Note that R_{avg} is the only parameter in $V_{\text{min}}(\theta)$ that depends on the ion size, and therefore electronic state of the complex.

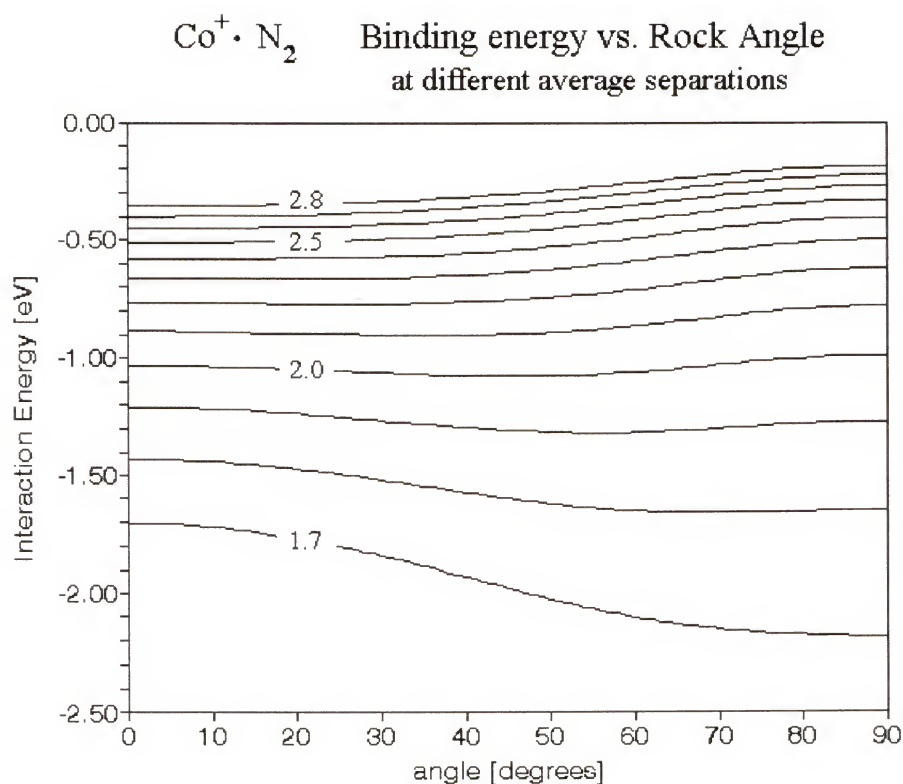


Figure 52. $\text{Co} \cdot \text{N}_2^+$ Binding Energy versus Rock Angle.

The figure shows a model of the interfragment potential energy of the $\text{Co}^+ \cdot \text{N}_2$ ion (in eV) versus rock angle for various choices of the average interfragment separation R_{avg} . The assumptions used to generate this potential appear in the text. This potential predicts a 'T'-shaped complex for small M^+ ionic radius and a linear one for larger radii.

Figure 52 shows a plot of $V_{\min}(\theta)$ versus θ using parameters appropriate to the CoN_2^+ complex for several choices of the average interfragment separation R_{avg} (shown in the figure in units of 10^{-8} cm). For small R_{avg} the model potential indicates that the inductive forces dominate over electrostatics and a T-shaped equilibrium geometry for the complex should be observed, just as is seen experimentally for the ground state. If the average internuclear separation increases substantially, however, as would happen upon optical excitation of a state of greater ion size, the longer ranged charge-quadrupole forces dominate and the molecule becomes linear.

In summary optical transitions in the $\text{Co}^+\cdot\text{N}_2$ ion complex have been observed and analyzed. The spectrum indicates that the states of the ion corresponding to the $3d^8$ configuration of the Co^+ are 'T'-shaped and those corresponding to the $3d^74s$ are linear. A simple model potential of electrostatic and inductive forces is sufficient to explain this behavior. This cluster appears to exhibit a delicate balance of forces and detailed study of the ro-vibronic structure of its various electronic states may provide insight into long-ranged forces between ions and molecules.

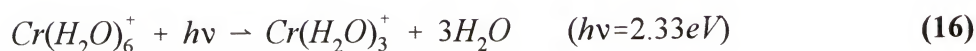
Hexaquo Chromium I Cation

The largest system discussed in this dissertation is the $\text{Cr}(\text{OH}_2)_6^+$ complex. The binding energy of water to the Cr^+ ion has been determined via the photofragmentation of $\text{Cr}(\text{OH}_2)_6^+$. Unlike the diatomics investigated in the previous chapter, the binding of the water to the chromium is governed primarily by charge-dipole and dipole-dipole interactions, which are long range in nature and behave like $1/r^3$ and $1/r^2$ respectively.

There are, of course, charge induced dipole terms, as before, as well as other multipole terms.

Binding energies for water(s) bound to several metal cations have been found using threshold for collision-induced dissociation (CID) or high pressure mass spectroscopy (HPMS). In particular Michl^{30,31} reports the binding energy for $\text{Cr}(\text{H}_2\text{O})^+$ as ca. 1.27 eV and Squires gives the binding energies for $\text{Cr}(\text{H}_2\text{O})^+$ and $\text{Cr}(\text{H}_2\text{O})_2^+$ as ca. 0.96 and 1.29 eV, respectively.

In this experiment the $\text{Cr}(\text{H}_2\text{O})_6^+$ was produced in a manner similar to the water systems produced above. The laser vaporized the surface of a chromium plated aluminum rod in the presence of water vapor seeded in the helium gas. The horizontal deflector was raised slightly so as to let this higher mass through the mass spectrometer. The photodissociation laser was set to a particular wavelength and then the voltage on the kinetic energy filter was tuned to allow various photofragments through to the detector. Scanning the voltage in this way with the photodissociation laser wavelength fixed, all photofragments of a particular parent ion could be observed. To selectively study $\text{Cr}(\text{H}_2\text{O})_6^+$, the dissociation laser is fired so that these ions are intersected just prior to entering the kinetic energy filter. Any photoproducts are detected at the MCP about 5 μs later. The following photodissociation processes are observed with second and third harmonic $\text{Nd}^{+3}:\text{YAG}$ fundamentals, respectively.



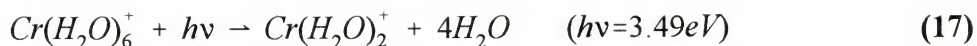


Figure 53 shows two kinetic energy filter scans, one with 40 mJ/pulse of 355nm light (dotted line) and the other with 65 mJ/pulse of 532nm light (solid line). The predominate products are clearly those indicated in eq. (16) and eq. (17). Additionally, attempts to observe resonant photodissociation across a majority of the visible spectrum yielded no discernable features but only constant dissociation background.

The observations are very persuasive evidence that $\text{Cr}(\text{H}_2\text{O})_6^+$ is a nearly black body for visible light. If this is the case, then two assumptions about the photodissociation process may be made to determine the binding energy per water in the complex. The first assumption is that the photodissociation process must be adiabatic. This seems reasonable due to the fact that the parent ions are very cold (ca. 2 to 10 K as shown in previous sections), the photodissociation process happens quickly (less than 4.5 μs) and the photoproducts are probably low energy. Second, the binding energy of each water is assumed to be approximately the same. This assumption is somewhat less likely than the first. The binding energy for the third water is probably higher than for the sixth. This has been the case in calculations of CoAr_n^+ and VAr_n^+ (discussed in Chapter 6) and for the previously mentioned CID experiments.

Regardless of any assumptions, there is a strong indication that the threshold for dissociation of four water molecules from the chromium ion lies between 2.33 and 3.49 eV or 2.91 ± 0.58 eV. Care must be taken to assign the observed threshold as the

adiabatic threshold, because the kinetics for the dissociation of a large cluster may be slower than the observer's time window (for this experimental apparatus the window is less than 10 μ s). The treatment of the kinetics of cluster evaporation and its effect on the observed fragmentation has been presented by Klots³². If $\text{Cr}(\text{H}_2\text{O})_6^+$ is small enough for the kinetic shift of the dissociation threshold to be insignificant and the binding energies of all of the dissociated waters are nearly equal, this would give an approximate binding energy of 0.74 eV for waters 3 through 6. These binding energies are lower than that reported by Michl for $\text{Cr}(\text{H}_2\text{O})^+$ or for $\text{Cr}(\text{H}_2\text{O})^+$ and $\text{Cr}(\text{H}_2\text{O})_2^+$ reported by Squires³³. They do seem reasonable, because as the number of repulsive terms from the dipole-dipole interaction add up (all the dipole-dipole terms for the first solvation shell will be repulsive) the binding energy for each additional water is decreased somewhat. Additionally, lower average binding energies of 0.57 eV reported for $\text{Na}(\text{water})_n^+$ where $n = 3$ to 6 as measured by HPMS³⁴ indicates a more subtle interaction between the open shell Cr^+ ion and the water ligands. This is a relatively crude method of determining the binding energy for the metal with n ligands. It is only an approximate method for obtaining data for these larger cation systems which have broad unresolved spectra. Experience indicates that the measurement of ligand binding energies by this nonresonant multiple-center photodissociation procedure is inherently unreliable and should be avoided. The bonding in transition-metal electrostatic complexes should be probed with more subtlety.

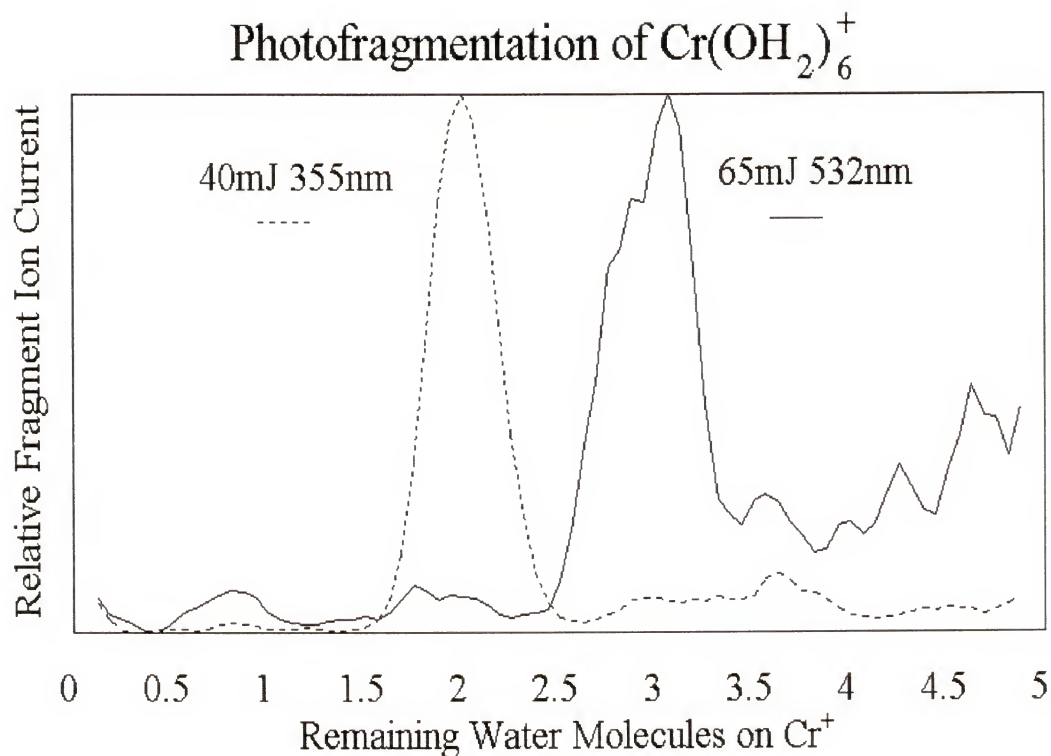


Figure 53. Relative Photofragmentation of $\text{Cr}(\text{OH}_2)_6^+$ with 532nm and 355nm Light.

The figure displays the relative photodissociation of the hexaquo chromium I cation with 532nm and 355nm light. The higher energy 355nm light causes all but two water molecules to be dissociated. The lower energy 532nm light causes the chromium ion to dissociate only three water molecules. The dissociation energy of each waters 3 through 6 is predicted to be ca. 0.74 eV.

Nickel Water Cation

The nickel water cation cluster with four atoms has a fairly simple spectrum which reveals the structure of ground and excited state. The structure of $\text{Ni}(\text{HOH})^+$ is much like formaldehyde, H_2CO , which has been fully studied by numerous groups³⁵. A few groups have reported results for the $\text{Ni}^+\cdot\text{H}_2\text{O}$ cation. Rosi and Bauschlicher^{36,37} have calculated ground state Ni-O bond length and strength in $\text{Ni}(\text{OH}_2)^+$ to be 1.975 Å (3.733 a_0) and 1.86 eV (42.8 kcal/mole) respectively. Marinelli and Squires³³ have investigated the $\text{Ni}(\text{HOH})^+$ cation as well and found D_0 to be 1.72 eV (39.7 kcal/mole). Michl et al.^{30, 31, 30, 31} have placed the value of D_0 at 1.58 eV (36.5 kcal/mole). The nickel-water cation is an interesting system for various reasons. It was the first electrostatically bound nickel system observed to have sharp spectral features. NiAr^+ , which had previously been thought to give only a featureless edge at 17984 cm^{-1} indicating the onset of a photodissociation threshold¹⁵. NiCO_2^+ has both features, sharp resonances and an abrupt edge, and has been discussed in a previous section. The first observed $\text{Ni}\cdot\text{OH}_2^+$ electronic origin occurs at 16800 cm^{-1} with vibrational and rotational structure built upon it. A second progression is observed at 18350 cm^{-1} and its vibrational and rotational structure extend to well beyond 20000 cm^{-1} . This observation encouraged the reinvestigation of the NiAr^+ reported in the previous chapter. Additionally, the kinetic isotope effect for the $\text{Ni}(\text{HOH})^+$ vs $\text{Ni}(\text{DOD})^+$ is the most pronounced seen in the Brucat Lab. $\text{V}(\text{HOH})^+$ vs $\text{V}(\text{DOD})^+$ had an observable cross section ratio³⁸ of at least 3:1 while the nickel counterparts have a ratio of ca 20:1 at the electronic origin. Duncan et al.⁶ study of $\text{Mg}(\text{water})^+$ do not mention any noticeable difference for the two isotopomers. Zare et

al.³⁹ have reported 25:1 and 1:8 OD:OH product ratios for the H + HOD(100) and H + HOD(001) reactions, respectively.

The transition which leads to photofragmentation in this complex is derived from a parity forbidden transition in the metal ion. As the electronic state arising from $\text{Ni}^+(3d^9)$ ^2D changes to the state arising from the $\text{Ni}^+(3d^84s)$ ^2F , various modes of vibration and rotation become active. Photodissociation occurs as these modes couple to a dissociative state resulting in this simple photodissociation reaction.



The metal ion electronic configuration in the upper state of the transition has a larger repulsive interaction with the 'ligand' in the complex which results in an increase in ion-ligand equilibrium separation and a long progression in the symmetric stretching mode in the absorption spectrum of the cold ion. Figure 54 shows a portion of the photodissociation action spectrum of $^{58}\text{Ni}(\text{H}_2\text{O})^+$ for the region from 16600 cm^{-1} to 20400 cm^{-1} . The isotopomers $^{60}\text{Ni}(\text{H}_2\text{O})^+$, $^{58}\text{Ni}(\text{H}^{21}\text{HO})^+$ and $^{58}\text{Ni}(\text{H}_2^{18}\text{O})^+$ have been scanned as well, to assign the electronic origins. No H_2O^+ , NiO^+ , or NiOH^+ photofragments are observed at these photon energies.

The $\tilde{A}$ excited state progression, shown in Figure 55, with a beginning at ca. 16600 cm^{-1} has a vibrational frequency, ω_e , of 349.9 cm^{-1} and an anharmonicity, $\omega_e x_e$, of 2.78 cm^{-1} . The nickel isotope shifts indicate that the origin of the vibrational, T_{e0} , is 16715 cm^{-1} . The assignment of this first excited state origin is made simpler by the fact that the adiabatic expansion has cooled the $\text{Ni}(\text{HOH})^+$ into the vibrationless ground

$\text{Ni} \cdot \text{OH}_2^+$ Photodissociation

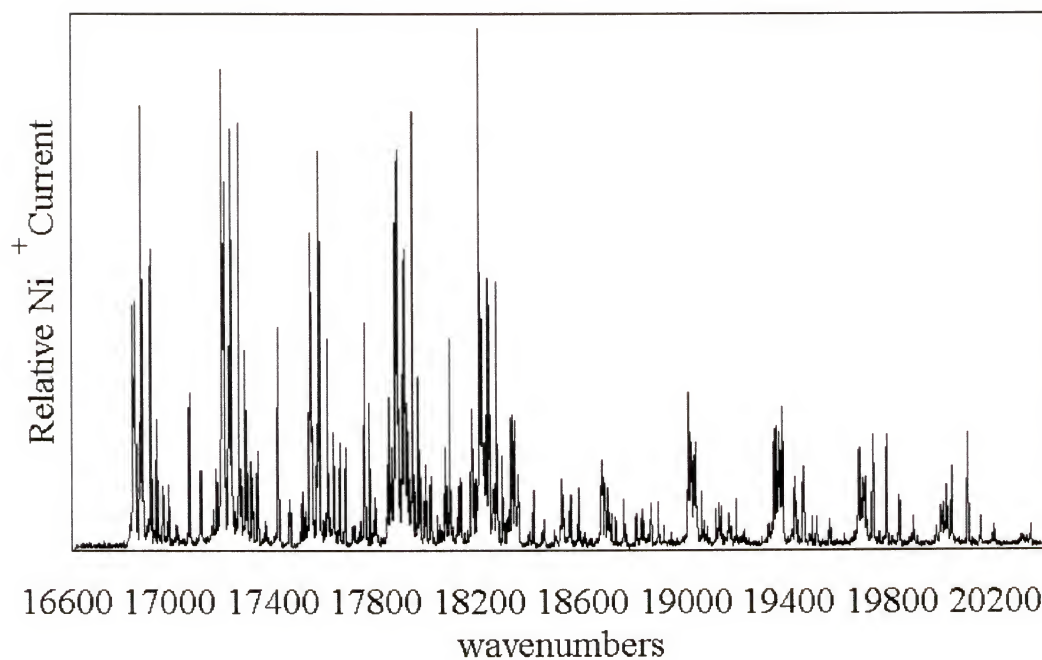


Figure 54. Photodissociation Spectrum of $\text{Ni} \cdot \text{OH}_2^+$.

The figure shows the photodissociation action spectrum for $\text{Ni} \cdot \text{OH}_2^+$. The vertical axis is the relative Ni^+ current from the fragmentation of the parent ion. The figure is a compilation of scans covering the region of 16600 to 20400 cm^{-1} . There are at least two vibrational progressions in this region, each of which has J and K rotational structure.

$\text{Ni} \cdot \text{OH}_2^+$ Photodissociation

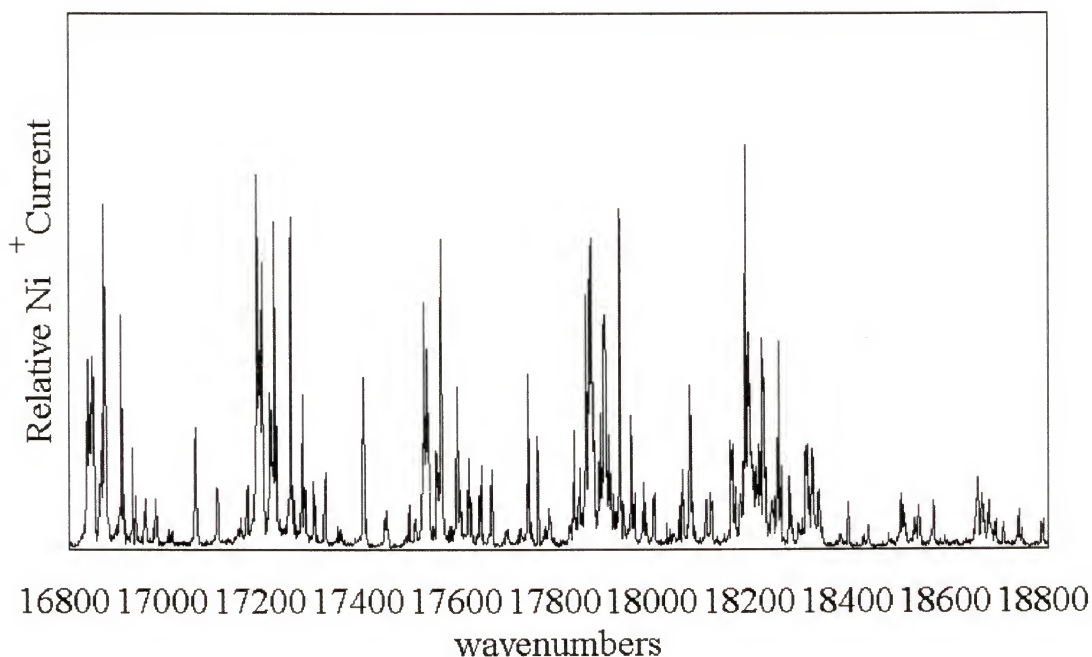


Figure 55. $\text{Ni} \cdot \text{OH}_2^+$ $\tilde{\text{A}}-\tilde{\text{X}}$ Transitions.

The figure shows a portion of the photodissociation action spectrum for $\text{Ni} \cdot \text{OH}_2^+$ covering the region of 16800 to 18800 cm^{-1} . The K rotational structure of the $\tilde{\text{A}}$ state is clearly evident on even this large scale. The $\tilde{\text{A}}$ state origin is at ca. 16715 cm^{-1} vibrational constant, ω_e , is 349.9 cm^{-1} , with an anharmonicity of 2.78 cm^{-1} .

$\text{Ni} \cdot \text{OH}_2^+$ Photodissociation

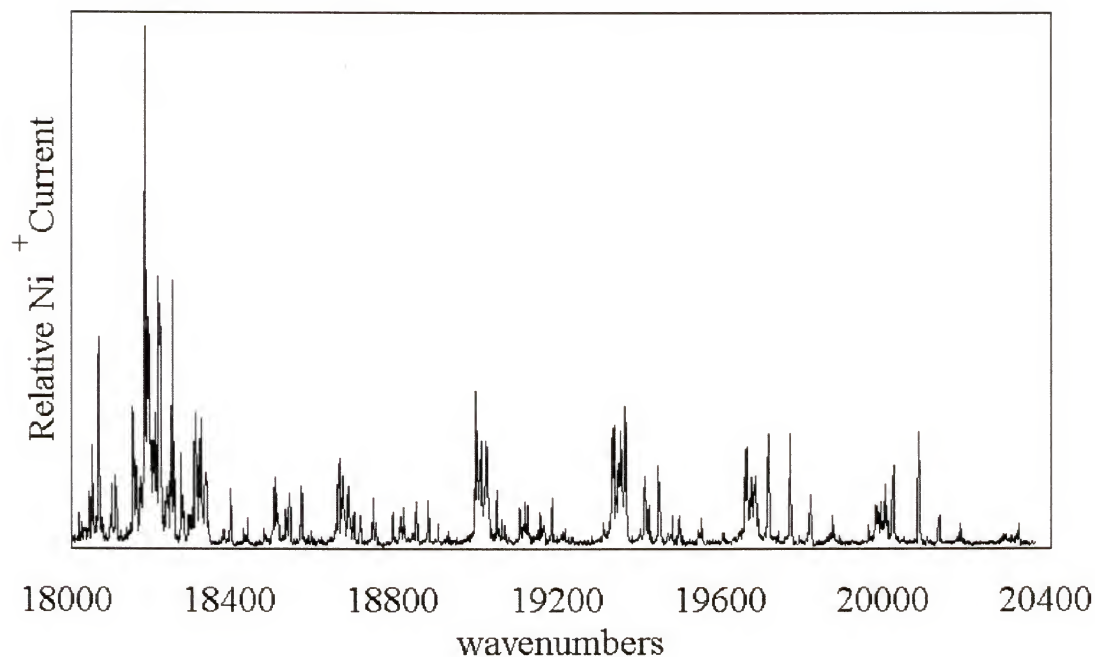


Figure 56. $\text{Ni} \cdot \text{OH}_2^+$ $\tilde{\text{B}}-\tilde{\text{X}}$ Transitions.

The figure shows the $\tilde{\text{B}}$ state for $\text{Ni} \cdot \text{OH}_2^+$ covering the region of 18000 to 20400 cm^{-1} . The K rotational structure of the $\tilde{\text{B}}$ state is clearly evident in this figure as well. The $\tilde{\text{B}}$ state origin is at ca. 18150 cm^{-1} vibrational constant, ω_e , is 348.0 cm^{-1} , with an anharmonicity of 2.45 cm^{-1} .

$\text{Ni} \cdot \text{OH}_2^+$ Rotational Detail

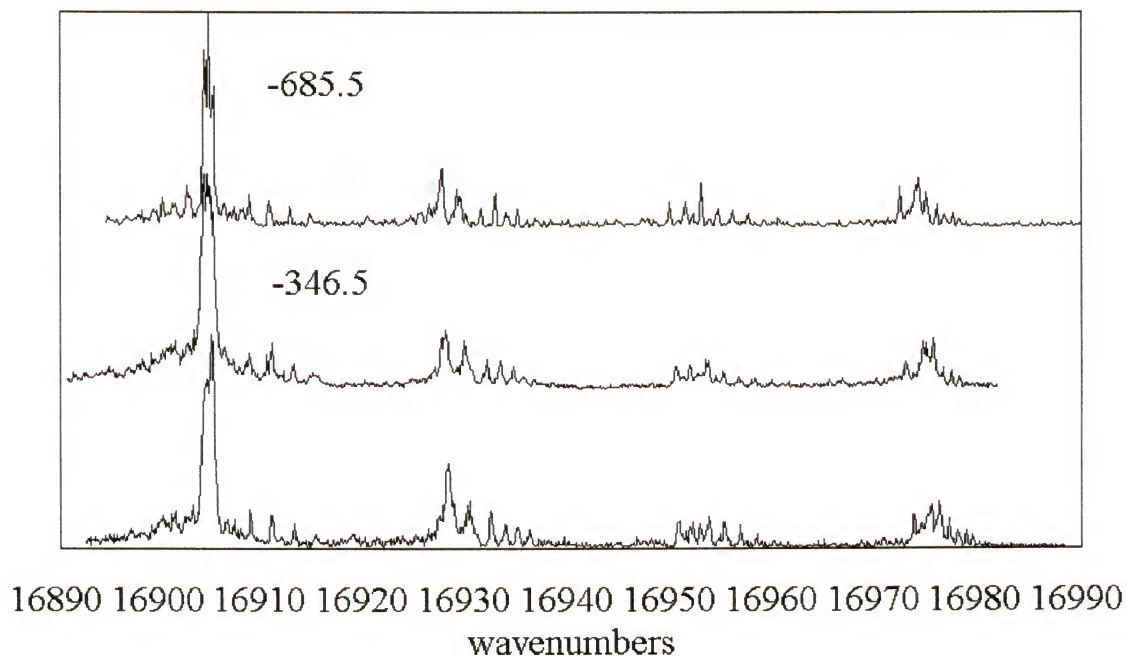


Figure 57. Rotational Structure of Three $\text{Ni} \cdot \text{OH}_2^+$ $\tilde{\text{A}}-\tilde{\text{X}}$ K Bands.

The figure shows three $\tilde{\text{A}}$ state rotational scans for $\text{Ni} \cdot \text{OH}_2^+$ the lowest trace is of the $\tilde{\text{A}}-\tilde{\text{X}} (0,0) \Delta K = +1$ band, the middle trace is the $\tilde{\text{A}}-\tilde{\text{X}} (1,0)$ shifted by -346.5 cm^{-1} and the upper most is the $\tilde{\text{A}}-\tilde{\text{X}} (2,0)$ shifted by -685.5 cm^{-1} . Each sub-band has J rotational structure built upon it.

electronic state. All of the vibrational transitions are therefore $v' \leftarrow v'' = 0$ and are labeled in $(v', 0)$. The reader may note that in the rotational analysis there are some rotational bands arising from rotation in the ground electronic state.

The $\tilde{B}$ excited state progression, shown in **Figure 56**, beginning at 18300 cm^{-1} has a vibrational frequency, ω_e , of 348.0 cm^{-1} and an anharmonicity, $\omega_e x_e$ of 2.45 cm^{-1} . The nickel isotope shifts indicate that the origin of the vibrational, T_{e0} , is 18150 cm^{-1} . As in the previous state all observed transitions arise from the vibrationless ground state. Both these states need to be fit to rotational contours which model their J and K substructure to get exact vibrational constants.

There are basically two types of rotational information which we can obtain from our data, because $\text{Ni}(\text{H}_2\text{O})^+$ is nearly a prolate symmetric top ($I_A < I_B \sim I_C$). The line positions are given by the familiar formula from Herzberg³

$$F(J,K) = BJ(J+1) + (A-B)K^2 \quad (19)$$

where A and B are rotational constants and J and K are the rotational quantum numbers. Closer inspection of **Figure 55** or **Figure 56** reveals K structure built upon each of the vibrational quanta of both excited states. The expanded view of the $\Delta K = +1$ of $\tilde{A}-\tilde{X}$ (0,0) in the lowest trace of **Figure 57** gives a clearer view of this structure. Additionally, the K levels display J structure in **Figure 57** which displays the $\Delta K = +1$ bands of $\tilde{A}-\tilde{X}$ (0,0), $\tilde{A}-\tilde{X}$ (1,0), and $\tilde{A}-\tilde{X}$ (2,0). The change in this structure from one K stack to the next is small but is clearly visible on this large scale.

Chopping the spectrum of the first excited state into sections of ω_e and stacking and offsetting the pieces, the change in both the J and K structure with increasing v' , **Figure 58**, are directly observable. The collapsing K structure tells us that as v' increases the A rotational constant of the upper state is decreasing. Comparing the K structure of $^{58}\text{Ni}(\text{}^1\text{H}_2\text{O})^+$ to the $^{58}\text{Ni}(\text{}^1\text{H}^2\text{HO})^+$ or $^{58}\text{Ni}(\text{}^2\text{H}_2\text{O})^+$, shows the effect of changing the isotope. New bands become allowed by symmetry for the asymmetric substituted species, the symmetric deuterated species has collapsing K structure merely from the increase of the effective reduced mass.

The geometry of the $\tilde{\text{A}}-\tilde{\text{X}}$ and $\tilde{\text{B}}-\tilde{\text{X}}$ electronic transition may be determined from the fit to the rotational structure for each of the observed vibrational quanta for the various isotopomers. The rotational fit for this molecule is slightly more difficult than that for those previously outlined in this text, and is currently being investigated.

The nickel water cation has provided much more detail than previously available for similar species (ie. $\text{Mg}(\text{H}_2\text{O})^+$, $\text{V}(\text{H}_2\text{O})^+$ and $\text{Sr}(\text{H}_2\text{O})^+$). These details will enable us to determine what the potential energy surface (PES) for the interaction may be. This PES will govern the dynamics of the $\text{Ni}(\text{H}_2\text{O})^+$ complex. This complex differs from similar transition metal-rare gas cations in that the ligand has a permanent electric dipole. The primary interaction is the charge-permanent dipole. There are other terms in the interaction such as the charge induced dipole and van der Waals, however, these will be much smaller in magnitude.

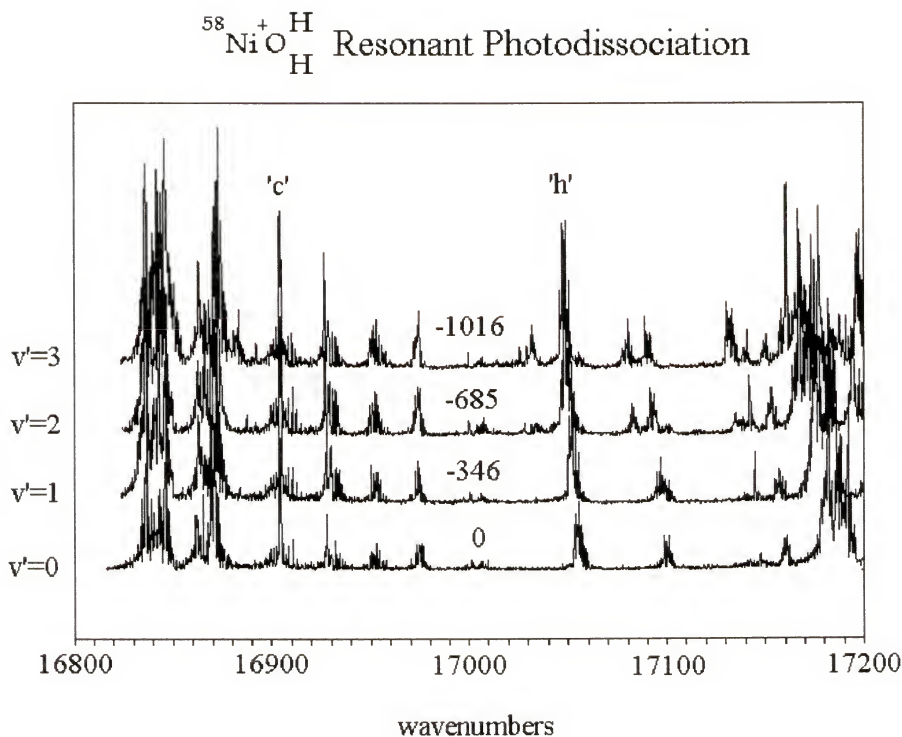


Figure 58. $\text{Ni}\cdot\text{OH}_2^+$ $\tilde{\text{A}}$ State Overlapping Spectrum.

The figure shows an overlapping spectrum for $\text{Ni}\cdot\text{OH}_2^+$ covering the first few vibrational levels of the $\tilde{\text{A}}$ state. The $\tilde{\text{A}}$ state origin is at ca. 16715 cm^{-1} vibrational constant, ω_e , is 349.9 cm^{-1} , with an anharmonicity of 2.78 cm^{-1} . Each trace is offset by ca. ω_e from the previous. This type of overlap spectrum gives a great deal of insight into the structure of the complex.

The charge-dipole interaction is a starting point for understanding more complicated solvation interactions. There is much information to be extracted from the data present in this dissertation. Not only do should it be possible to know the spacing of the vibrational lines, it should be possible to know how the rotational constants (A, B and perhaps C) change as v' increases and thus a potential energy surface. This all depends upon correct fitting of the rotational data.

Cobalt Water Cation

Our group began its study of electrostatically bound ion-water complexes³⁸ with $V(OH_2)^+$. $Co(OH_2)^+$ is comparable to this system, however, much more information about this new system is available because of the spectroscopic detail. Various experimental groups have investigated singly charged ions interacting with one or more water molecules as mentioned in the nickel water section. Spectroscopic analysis of $Mg(H_2O)^+$, by Duncan et al.⁶, has revealed some detail about its structure and geometry.

Rosi and Bauschlicher^{36,37} have predicted the ground state of $Co(H_2O)^+$ as $^3B_2$ with the Co^+-O bond length of 1.99Å and a bond energy of 1.73eV.

Simultaneous scanning of all three, $Co(OH_2)^+$, $Co(OHD)^+$ and $Co(OD_2)^+$, isotopomers and the output of a capacitively coupled optogalvanic cell insure accurate isotope shift data ($\pm 0.1\text{ cm}^{-1}$) and spectral calibration ($\pm 1.5\text{ cm}^{-1}$). Such a scan is shown in Figure 59, which shows four electronic states over the region from 13200 cm^{-1} to 18200 cm^{-1} . Better insight into the spectrum can be obtained using the method of overlapping discussed in previous sections. The first two states have been expanded to

$\text{Co}(\text{OH}_2)^+$ Photodissociation

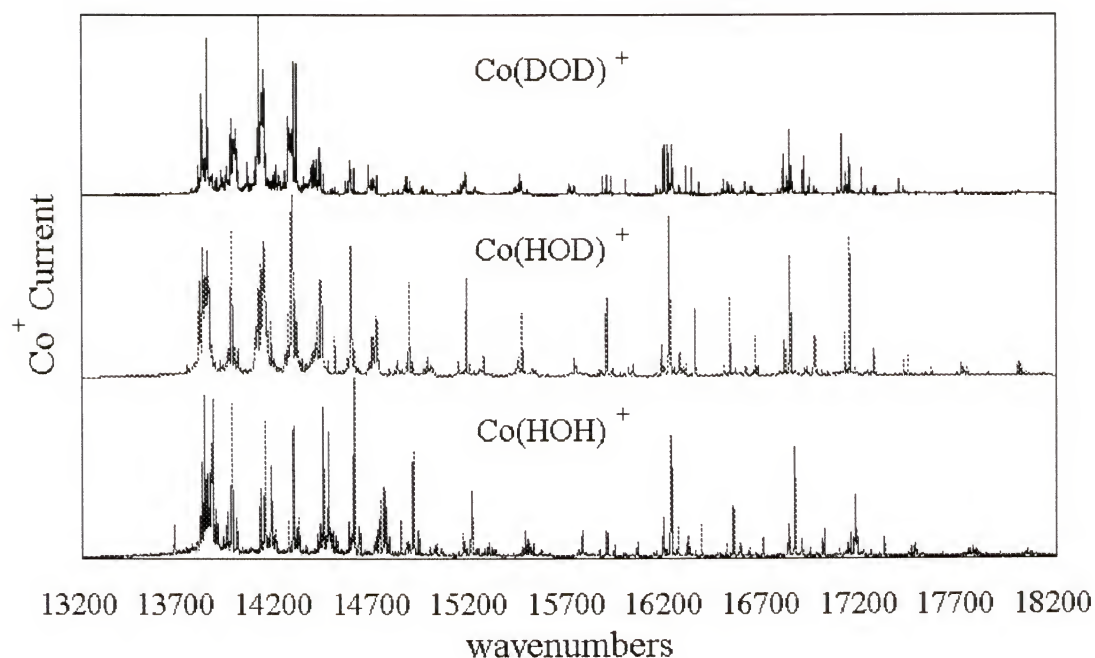


Figure 59. $\text{Co}\cdot\text{OH}_2^+$ Photodissociation Spectrum.

The figure shows a portion of the $\text{Co}\cdot\text{OH}_2^+$ spectrum over the region of 13200 cm^{-1} to 18200 cm^{-1} . The three traces are from the three isotopes of water, H_2O , HOD , and D_2O , bound to the Co^+ . The vertical axis is the relative cobalt cation current coming from the three isotopomers. There are four electronic states in the region above, and these have been labeled for $\tilde{\text{A}}$, $\tilde{\text{B}}$, $\tilde{\text{C}}$, and $\tilde{\text{D}}$.

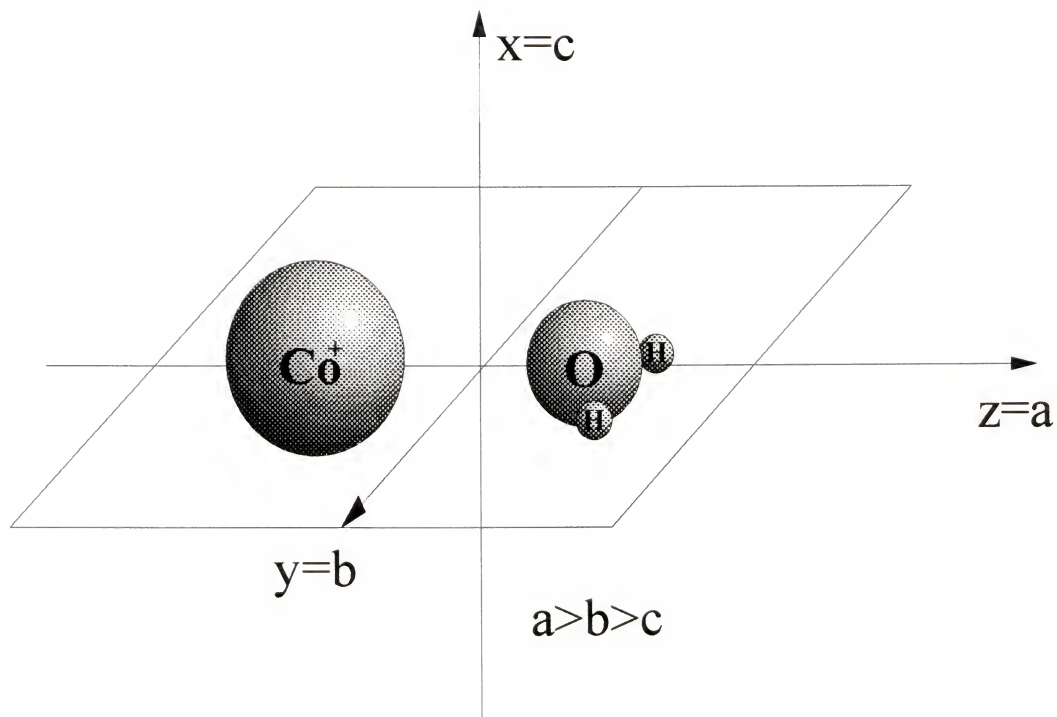


Figure 60. $\text{Co}(\text{H}_2\text{O})^+$ Symmetry.

The figure shows the $\text{Co}(\text{H}_2\text{O})^+$ in the primary axis. The symmetry is C_{2v} and the hydrogens make the molecule a nearly prolate top.

$\text{Co}\cdot\text{OH}_2^+$ Photodissociation

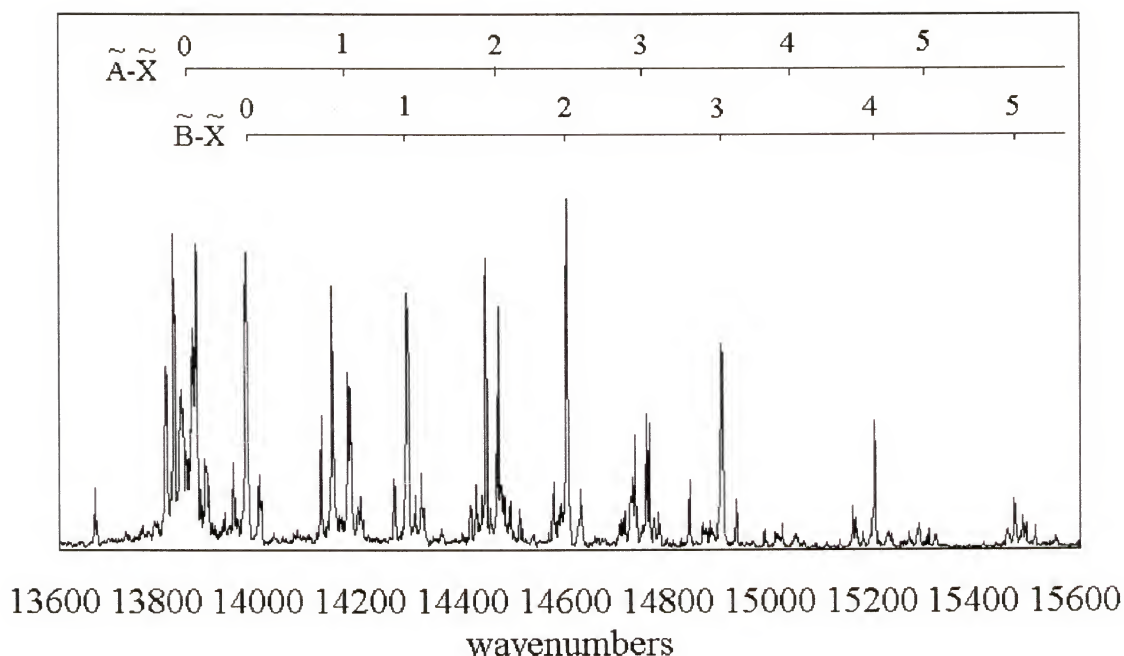


Figure 61. $\text{Co}\cdot\text{OH}_2^+$ $\tilde{\text{A}}-\tilde{\text{X}}$ and $\tilde{\text{B}}-\tilde{\text{X}}$ Electronic Transitions.

The figure shows a blowup of $\text{Co}\cdot\text{OH}_2^+$ shown in Figure 59 for the region from 13600 cm^{-1} to 15600 cm^{-1} . The only trace is H_2O bound to the Co^+ . The vertical axis is the relative cobalt cation current. The two electronic states indicated in the region above labeled $\tilde{\text{A}}$ and $\tilde{\text{B}}$ have different ω_e 's and rotational structure. The isotope shift from the D_2O and HOD have enabled the absolute vibrational numbering of the levels, and the origin of both states is evident.

show the progressions labeled $\tilde{A}-\tilde{X}$ and $\tilde{B}-\tilde{X}$. These four electronic states have been fit to simple diatomic anharmonic to give the stretching frequencies. These have been plotted for the HOH, HOD and DOD isotope. The change in ω_e follows a general trend with the reduced mass and is displayed in **Figure 62**.

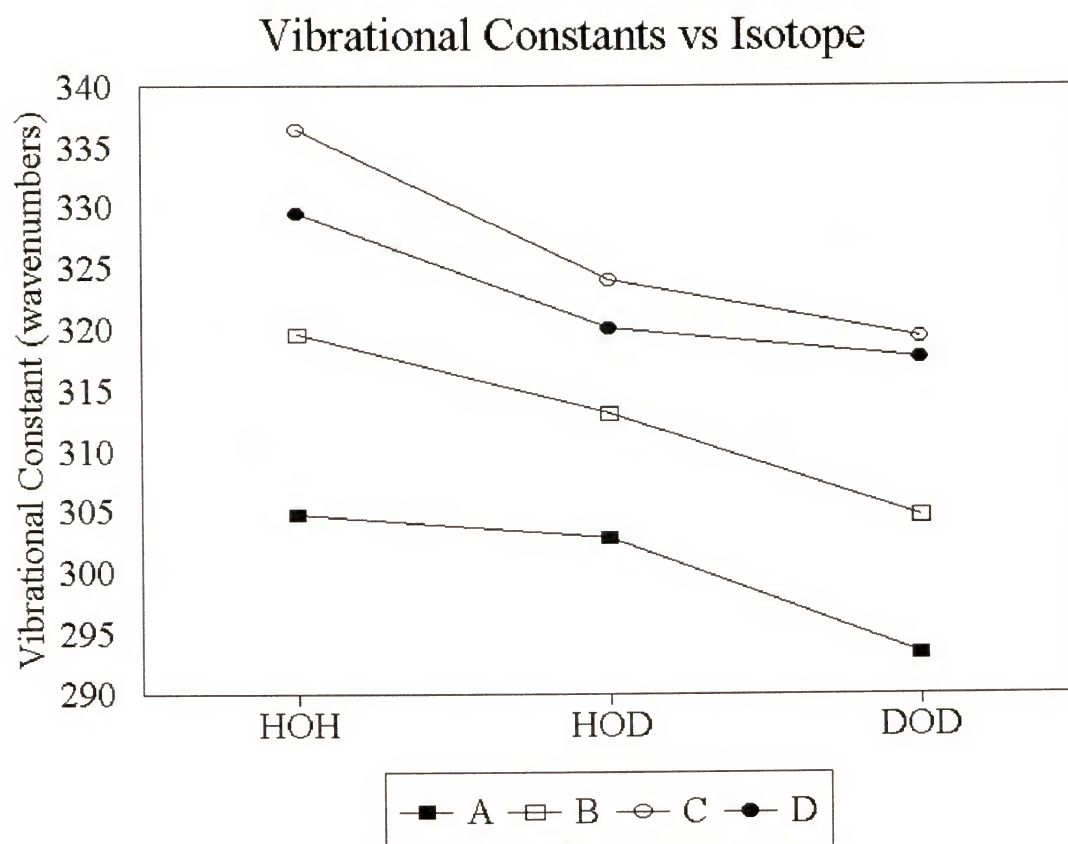


Figure 62. $\text{Co}\cdot\text{O}^1\text{H}_2^+$, $\text{Co}\cdot\text{O}^1\text{H}^2\text{H}$ and $\text{Co}\cdot\text{O}^2\text{H}_2$ $\tilde{\text{A}}$, $\tilde{\text{B}}$, $\tilde{\text{C}}$ and $\tilde{\text{D}}$ ω_e

The figure shows the simple anharmonic oscillator fit ω_e 's obtained for cobalt cation $\tilde{\text{A}}$, $\tilde{\text{B}}$, $\tilde{\text{C}}$ and $\tilde{\text{D}}$ have different ω_e 's plotted against the various water isotopes. As the weight of the water isotope increases, the stretching frequency decreases as is expected.

CHAPTER 5

TWO-COLOR PHOTODISSOCIATION

The experimental chapter briefly explained that two tunable dye lasers could be used in conjunction to do two-color spectra of molecular ions. There are two types of two-color experiments which can be carried out in the current setup, resonant two-color dissociation (R2CD) and stimulated emission pumping (SEP). To date we have been unsuccessful in accomplishing the latter, however, the former has given a greater insight into the nature of the Ni_2^+ species. Previously resonant two photon dissociation (R2PD) was used to investigate several states in the Ni_2^+ system⁴⁰, however, R2CD gives a much better picture of what is happening.

The bonding between transition metal atoms has been characterized spectroscopically for numerous transition-metal dimer and some trimer systems.⁴¹ Direct spectroscopic data from these molecules yields the most complete characterization of the bonding, however, the majority of the data on these systems comes from other techniques. Thermochemistry of bonding in isolated metal containing cations has been made possible by clever high pressure mass spectrometry^{42,43} and guided ion beam technology⁴⁴. Direct optical study of cationic molecules can in principle provide great detail of the bonding in these systems, however, even few transition-metal ions have suffered high-resolution spectral probes. Most notable counter examples are the recent determination of

photodissociation thresholds in transition metal diatomic ions (Co_2^+ , Ti_2^+ , and V_2^+) by pulsed laser excitation of the cold isolated ion in a tandem mass spectrometer⁴⁵. These ion photodissociation thresholds have been found to be 'sharp' and may be trivially interpreted as the onset of the adiabatic limit for dissociation into ground state fragments, i.e the threshold directly indicates D_0 of the ground state of the molecule. Ni_2^+ is an example that not all transition metal cations behave in this way.

Ni_2^+ Bond Strength

The bonding in Ni_2 has been the focus of some considerable experimental and theoretical attention and serves as a model of late transition-metal bonding. The electronic spectrum of this neutral has been obtained by multi-photon ionization (MPI) and the bond strength (D_0) of 2.068 ± 0.001 eV determined from the onset of rapid predissociation at the adiabatic bond dissociation energy⁴⁶⁴⁶ in a similar fashion to the ion studies described above. Although this measurement strictly speaking only gives an upper limit to D_0 , the abrupt decrease in excited state lifetime at this energy along with the large density of interacting electronic states leads to the conclusion that this threshold is probably very close to the adiabatic limit.

The Ni_2^+ ion has also been the object of direct spectroscopic probes⁴⁰. Its bond energy, however, has not been bounded spectroscopically until this work. Estimates of the bond strength derived from the energy dependent branching ratio of the photoproducts of Ni_2Ar^+ (3.0-3.5 eV⁴⁷) and the much more established threshold collisional dissociation method (2.08 ± 0.07 eV⁴⁴) are found to be in disagreement. *Ab*

initio theory⁴⁸ predicts a $^4\Sigma_g^+$ ground state for the ion with a dissociation energy of 1.86 eV. The theoretical result is expected to be low but the relative bond strengths in Ni_2 and Ni_2^+ from the same level of calculation is expected to be more accurate. The ion and neutral bond strengths are shown to be similar by this argument, with the ion being more strongly bound than the neutral by 0.17 eV. The small increase in bond strength upon ionization of the molecule predicted by theory supports the CID study and the lower bond energy.

This investigation of the photodynamics of levels in Ni_2^+ which are more than 2 eV above the ground state provide a hard upper limit to the bond strength (D_0) of 2.34 eV. This corresponds to an energy where the first one-photon dissociation of the cold ions is observed. Arguments similar to that made in the determination of the bond strength for Ni_2 lead one to conclude that the adiabatic bond strength should be within one vibrational quantum of this upper limit, leading to the value for D_0 for Ni_2^+ of 2.32 ± 0.02 eV.

Figure 63 (bottom panel, labeled R2CD) shows a portion of the resonant two-color photodissociation spectrum of Ni_2^+ . This spectrum should be about as close to the actual absorption spectrum of this molecule as one can get for an isolated ion. The horizontal axis is transition frequency (in cm^{-1}) of the first (resonant) laser field (<5 $\text{mJ}/\text{cm}^2\cdot\text{pulse}$; 0.1 cm^{-1} FWHM bandwidth) and the vertical axis is relative dissociation of the ion (Ni^+ photocurrent). The resonant dissociation of the ions photoexcited by the tunable laser is enhanced by a fixed frequency laser pulse (frequency ≈ 15700 cm^{-1} ; 25-50 $\text{mJ}/\text{cm}^2\cdot\text{pulse}$) delayed by 10 ns (just greater than the pulse width of either laser) from

Ni_2^+ Photodissociation

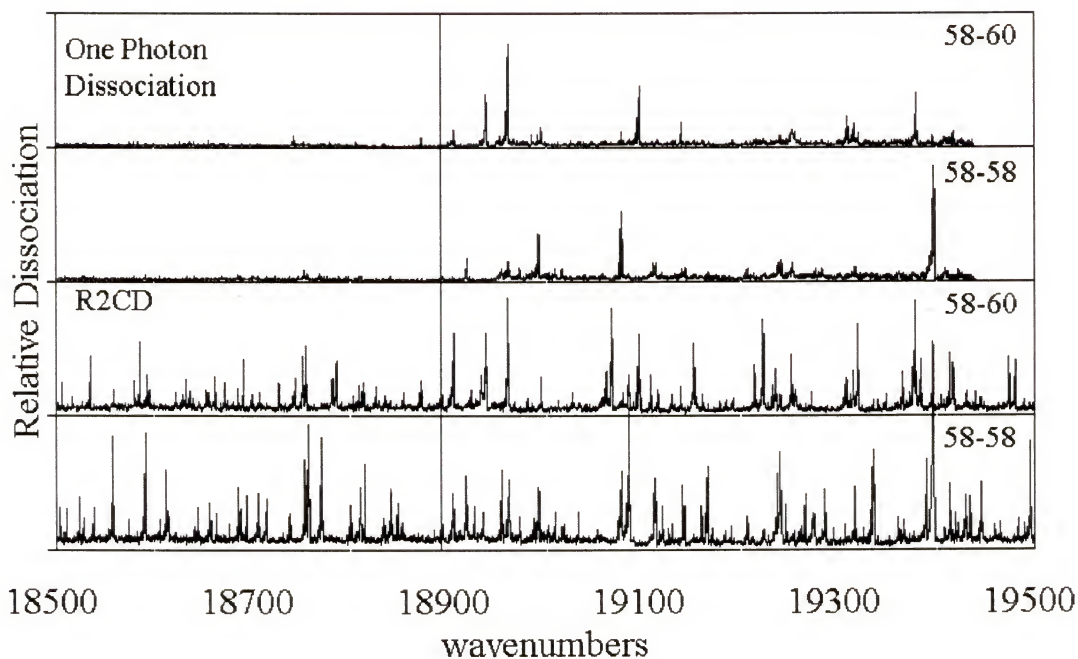


Figure 63. Ni_2^+ Two-color Photodissociation.

The figure shows the resonant dissociation spectrum of two isotopes of Ni_2^+ taken under two different sets of conditions. The top panel shows the spectrum obtained under conditions that favor the detection of one-photon dissociation events and is labeled as such. The bottom panel, taken with a low power resonant laser and a high-power non-resonant laser, should be close to the appearance of the true absorption spectrum and is labeled R2CD. In each panel the top trace is the spectrum of the isolated $^{58}\text{Ni}^{60}\text{Ni}^+$ isotopic species and the lower trace is the $^{58}\text{Ni}_2^+$. The onset of one photon dissociation occurs in all isotopes near 18900 cm^{-1} , which is indicated by the dashed vertical line. Thus, the dissociation limit, D_0 , of the molecule must lie near or below this value or $2.32 \pm 0.02\text{ eV}$.

the resonant laser. The second laser frequency is chosen to be non-resonant with cold parent ions. Since the parent Ni_2^+ ion is mass selected in the TOF, the photofragmentation of all the isotopomers of the Ni_2^+ molecule are obtained simultaneously in separate integration channels for each laser scan. The lower trace of the bottom panel shows the spectrum of $^{58}\text{Ni}_2^+$ spectrum which is the major isotopic species. The upper trace in each panel shows the photodissociation action spectrum of the heavier $^{58}\text{Ni}^{60}\text{Ni}^+$ isotopomer. (Secondary mass resolution of our mass spectrometer is insufficient to differentiate the $^{60}\text{Ni}^+$ versus $^{58}\text{Ni}^+$ fragments from this parent so the dissociation plotted is the sum of all fragmentation products.) As the ions in the beam are internally cold ($T_R < 10\text{K}$), all the peaks in this spectrum are transitions originating from the vibrationless ground state. Thus the transition frequency is simply the upper state energy above the zero point of the molecule. Rotational structure of these bands is obscured at this plot resolution but has been analyzed in the next section. This spectrum is typical of the entire visible region for this molecule with overlapping upper state vibrational progressions from several electronic transitions evident. Spectral shifts between the isotopes are useful in the determination of the absolute vibrational numbering of the bands. Assignment of this portion of the spectrum is omitted for clarity and is essentially irrelevant for the following arguments.

The R2CD spectrum in the bottom panel of **Figure 63**, although complicated and congested in appearance, shows no hint of unusual upper state dynamics. One may have predicted that the appearance of the spectrum should change abruptly once rapid coupling to the dissociative continuum is reached, just as is found in Ni_2 neutral⁴⁶ and in many other transition metal diatomic species⁴⁹. Yet the R2PD spectrum in this ion is sharp and

relatively well behaved in this energy region which is well above the dissociation limit predicted by theory⁴⁸ or estimated by CID⁴⁴. The fact that the spectrum did not show any unusual features at this energy⁴⁰ gave credence to the possibility of a large binding energy in Ni_2^+ . However, a more careful look at the lifetimes of the states in this energy range has revealed that the dissociation limit is indeed below 2.34 eV.

The lifetime of the excited states produced by the resonant laser may be estimated by the dependence of the dissociation yield as a function of delay between the first and second laser pulses. The dissociation is a maximum when the two lasers are almost simultaneous in time and decay time between the pulses is increased, confirming a sequential two-photon mechanism for most of the transitions in the bottom panel of **Figure 63**. The dissociation decay curves observed are non-exponential in time and depend somewhat on the color of the non-resonant (dissociation) laser. This is indicative of a radiative cascade process contributing to the stabilization of the photoexcited ion and somewhat complicates the extraction of the precise lifetime of the excited state. However, the time scale for the shortest component of the decays observed for all levels excited to the red of 18900 cm^{-1} is $\geq 1\text{ }\mu\text{s}$. Above 18900 cm^{-1} excited states with much shorter lifetimes are observed. Moreover, some transitions show virtually no enhancement in dissociation yield with the addition of a second laser pulse implying an excited state lifetime significantly shorter than the pulse width of our lasers (ca. 7 ns). These levels dissociate after the absorption of the resonant laser pulse alone, and therefore are above the adiabatic dissociation limit of the molecule.

An appropriate way to depict the appearance of short lived excited states is to compare the one-photon dissociation yield with the total absorption spectrum (or R2CD in this case). **Figure 63** shows such a comparison; the top panel shows the photodissociation action spectrum under the influence of the low-power resonant laser field only, the bottom panel shows the photodissociation under conditions that should mimic the absorption spectrum (R2CD, described above).

Clearly, the onset of strong one-photon dissociation transitions would indicate a threshold for a dissociation mechanism. The lowest energy transitions that lead to one-photon dissociation are found just above 18900 cm^{-1} for all isotopic variants of Ni_2^+ , and increase in occurrence to higher energy. If this is the lowest energy mechanism for dissociation, then this behavior indicates the threshold for adiabatic dissociation, D_0 is 18900 cm^{-1} .

It is now well demonstrated that the behavior of the photodissociation of transition metal diatomic neutrals and cations is widely varied in the region of the adiabatic dissociation limit. Sometimes, a sharp onset of continuous (or nearly continuous) absorption marks the bond energy⁴⁹, and sometimes, as in the case of Ni_2^+ , this limit only manifests itself in the excited state dynamics of a fraction of the optically accessible levels.

The bond strength of Ni_2^+ is found to be 0.25 eV greater than that of neutral Ni_2 , in reasonable agreement with the *ab initio* prediction⁴⁸ of an increase of 0.17 eV. This is at odds with the CID result⁴⁴ that indicates approximately the same bond strength in both molecules. Of course, as this study provides strictly only an upper limit, a lower value for the dissociation cannot be completely ruled out.

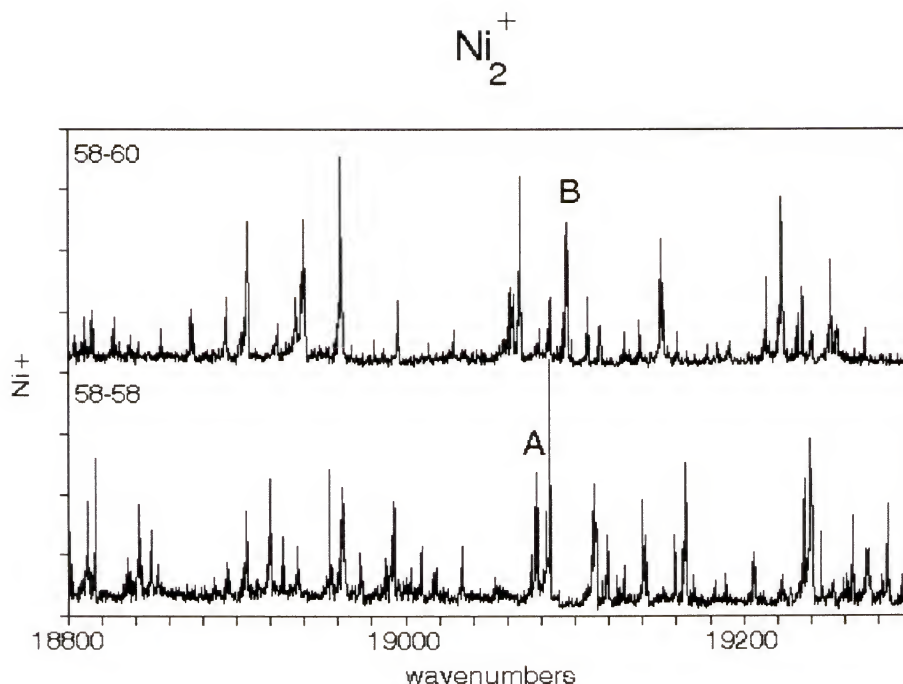


Figure 64. Ni_2^+ Two-color Photodissociation.

The figure shows the appearance of the Resonant Two-color photoDissociation (R2CD) spectrum of Ni_2^+ spectrum in the region between 18 800 and 19 300 cm^{-1} . The spectra of two isotopic species of this molecule, the $^{58}\text{Ni}_2^+$ and $^{58}\text{Ni}^{60}\text{Ni}^+$ ions, have been recorded simultaneously and are displayed in the lower and upper traces, respectively. Plotted on the vertical axis is the relative dissociation yield as monitored by the Ni^+ photocurrent, and on the horizontal axis is the frequency of a low power resonant laser which excited the ions with one photon. Following this, a high power (50 mJ/cm^2 -pulse) non-resonant laser dissociates excited ions, enabling the detection of transitions with bound or metastable excited levels. Two bands, labeled A and B, will be discussed in greater detail..

Ni₂⁺ Bond Length

An enlargement of **Figure 63** shows an interesting portion of the photodissociation action spectrum of the Ni₂⁺, **Figure 64**, with bands labeled 'A' and 'B'. The upper panel corresponds to the 118 mass and the lower is the 116 of the most abundant isotopomers: ⁵⁸Ni₂⁺ and ⁵⁸Ni⁶⁰Ni⁺. The fragmentation is simply the only one allowed:



Further enlargement about 'A' shows a closeup of one of the red degraded bands, **Figure 65** indicating a change in geometry between the ground and excited state discussed in the previous section. This band is not like the others in this progression, its branch structure is not complete and is dominated by three major peaks. It is suggestive to note that there are just three changes in J possible for an allowed electric dipole transition. This band is the only one, to date, which exhibits this unique appearance. There are no corresponding bands of similar intensity distribution in any of the other isotopomers. The labels in **Figure 65** are the energy separations (in wavenumbers) between the lines.

Figure 66 indicates the intensity distribution for this band. The upper state of the excited transition excited in **Figure 65** is above the dissociation limit of the molecule, as indicated in the previous section. The molecule does not predissociate on the time scale of the experiment except for a single rotational level which is accidentally perturbed.

Unfortunately, neither the nature of this perturbation nor the identity of the perturbing

state has yet been identified. Regardless of the nature of the upper state, the frequency differences between the strong lines in **Figure 65** depend only upon the ground state rotational constant and thus the ground state bond length. If the difference between the single Q and P branch lines is denoted as x and y is the difference between the single R and Q branch lines then a system of two equations:

$$x = Q(J) - P(J+1) = F''(J+1) - F''(J) = B''(2J+2) \quad (21)$$

and

$$y = R(J-1) - Q(J) = F''(J) - F''(J-1) = B''(2J) \quad (22)$$

In this analysis the ground state rotational energy assumed to be that of a simple rigid rotor. The rotational constant of the ground state and upper state J' number (of the perturbed level) can be extracted from

$$B'' = \frac{x - y}{2} \quad (23)$$

and

$$J' = \frac{y}{x - y} \quad (24)$$

The vibrationally averaged ground state bond length is determined from the usual relation

$$r_0'' = \sqrt{\frac{h}{8\pi^2\mu c B''}} \quad (25)$$

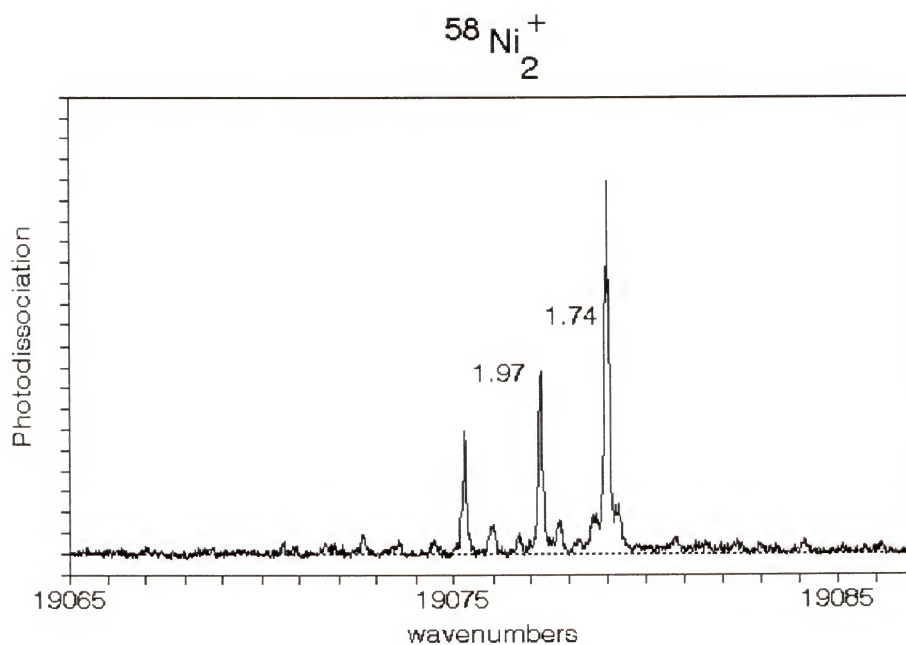


Figure 65. Ni_2^+ 'A' Band.

The figure shows the appearance of band 'A' in the R2CD spectrum of $^{58}\text{Ni}_2^+$ under somewhat greater resolution. This band shows an intensity anomaly resulting from a local perturbation of a single rotational level in the upper state. The separation between the three prominent features in the band are labeled in wavenumbers.

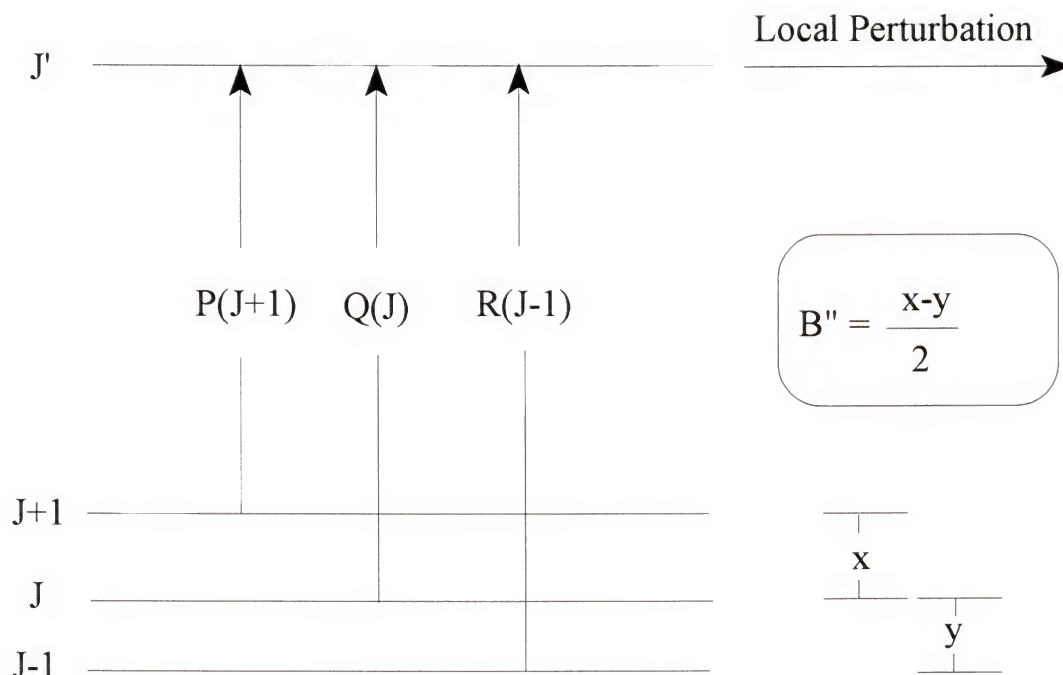


Figure 66. Ni_2^+ Perturbed State Schematic.

The figure depicts a scheme by which a single upper state rotational level which undergoes predissociation through the influence of a local "accidental" perturbation with a rapidly dissociating state. Usually such perturbations are unwanted, but in this case the detection of the dissociation action spectrum contains a pattern which is easily interpreted because it depends only upon the ground state rotational constant.

From **Figure 65**, the values of x and y (1.97 and 1.74 cm^{-1}) give a ground state rotational constant of 0.115 cm^{-1} for the $^{58}\text{Ni}_2$ molecule (reduced mass, $\mu = 28.9677\text{ g/mol}^{50}$) and thus a bond length of $r_0'' = 2.25 \pm 0.07\text{ \AA}$ for the ion. The uncertainty in the bond length comes from the uncertainty in a single triplet of line positions due to their laser-linewidth-limited breadth. These line positions also indicate that the upper state perturbation occurs at a rotational quantum number of $J' = 15/2$, but this information will not be of further use here.

All the bands in the spectrum arise from the vibronic ground state because the ions are internally cooled by supersonic expansion. Therefore, all the bands must (and do) show a consistent value of lower rotational constant. Moreover, the rotational constants of isotopic variants of the molecule must scale with inverse reduced mass (change in r_0 due to the change in vibrational wavefunction upon isotopic substitution is negligible in this case). **Figure 67** shows a complete band (labeled 'B' in **Figure 64**) observed by resonant two-color photodissociation (R2CD) of the $^{58}\text{Ni}^{60}\text{Ni}^+$ ion without the intensity anomaly of an accidental perturbation. Here the entire rotational contour is seen and simulated (lower trace) which yields the constants for both the upper and lower states. For band 'B', the bond lengths of the upper and lower states are 2.658 ± 0.005 and $2.225 \pm 0.005\text{ \AA}$, respectively. The rotational constants are more accurately determined than in the previous analysis because more transitions are involved in the determination.

More information is contained in the rotational contour than just the rotational constants. The simulation of the spectrum that has been generated is admittedly crude: a rigid symmetric top simulation for half-integral quantum numbers. The branch intensities

are expected to be somewhat inaccurate, but comparison with the observed spectrum yields an estimate of the rotational temperature of the ions in our beam, 7 K. This, of course, is not the first demonstration of ions cooled by supersonic expansion⁶, but it is gratifying that direct spectroscopic probes confirm low internal energy of the nascent parent ions in our technique.

The first lines in the three branches observed in the band 'B' spectrum are assigned as R(9/2), Q(9/2), and P(11/2) indicating an $\Omega'=9/2 \leftarrow \Omega''=9/2$ electronic transition. Perpendicular electronic transitions are observed in the R2CD spectrum as well. It is not possible at this resolution to distinguish between a doublet and a quartet ground state, nor is it possible to differentiate between a Hund's case (a) or case (c) description of the angular momentum coupling in the molecule.

The ground state predicted by *ab initio* theory⁴⁸ for this ion is a $^4\Sigma$ state with a bond length, r_e , of 2.244 Å and a bond dissociation energy, D_e , of 1.86 eV. Our band simulation clearly indicates $\Omega'' = 9/2$ which is inconsistent with this prediction even though the measured bond length of 2.225 ± 0.005 Å is in excellent agreement with theory. To be fair and accurate, Bauschlicher *et al*⁴⁸ do predict low lying $^2\Gamma_g$ ($r_e = 2.476$; $D_e = 1.610$ eV), $^4\Gamma_u$ ($r_e = 2.473$; $D_e = 1.673$), and $^4\Gamma_g$ ($r_e = 2.244$; $D_e = 1.82$ eV) states, all of which have an $\Omega = 9/2$ spin-orbit component. Of the choices, experiment seems to support the $^4\Gamma_g$ as the ground state symmetry of Ni_2^+ .

The properties of the nickel dimer cation are similar to those of the neutral molecule. It has been shown⁴⁶ that the ground state of Ni_2 is an $\Omega = 4$ state with a bond length of 2.200 Å and a bond strength of 2.092 eV which is consistent with either a $^1\Gamma_g$ or

$^3\Gamma_u$ ground state⁴⁸. The similarity in the bonding in the neutral and cation indicate that the d orbitals contribute negligibly to the bonding in both charge states and the ionization essentially occurs from the contracted d subshell. It is noteworthy that the ion has a slightly longer bond length than the neutral, contrary to what would be expected due to basis contraction. This behavior is inconsistent with the present level of theory as well as the symmetry and bond energy of the ground state. Still, some of the features of late transition metal bonding remains beyond the grasp of *ab initio* methods.

Lifetime of Ni_2^+

The lifetime of Ni_2^+ has been probed using via a two-color experiment, where a two-color peak is located, as in Figure 63, and then the time between the two dye laser pulses is varied. The result is an 'S'-shaped photodissociation intensity curve versus time between laser pulses and is displayed in Figure 68. The lifetime of Ni_2^+ is complicated by some type of relaxation mechanism. It is clear, from Figure 68, that the lifetime is shorter than 5000 ns for the peak in question. Several peaks in the Ni_2^+ have a somewhat shorter lifetime, and it was hoped that there would be a sharp change in this lifetime as the first photon energy changed from lower than the dissociation limit to above it. Figure 69 shows two possible cascade mechanisms which may lead to the behavior in Figure 68. The left panel shows the first photon energy above the dissociation limit, and the right shows it below. The rate determining step in Ni_2^+ is as yet unknown, and a full study using the techniques discussed in this dissertation do not seem adequate for more precision than given by the S-shaped curve in Figure 68. Either of these two schemes present

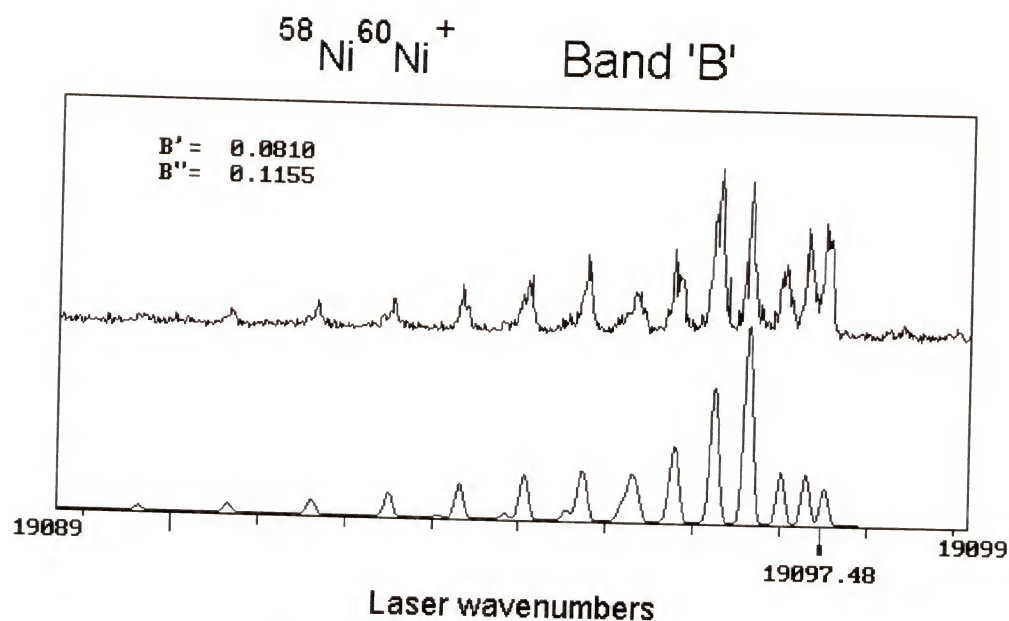


Figure 67. Ni_2^+ 'B' Band.

The figure shows the appearance of a complete rotational band in the $^{58}\text{Ni}^{60}\text{Ni}^+$ ion observed by R2CD. The top trace is an experimental spectrum and the bottom is a rigid symmetric top simulation of an $\Omega'' = 9/2$ to $\Omega' = 9/2$ transition at a temperature of 7 K. The simulation indicates a lower state rotational constant 0.1155 cm^{-1} and an upper state rotational constant of 0.088 cm^{-1} .

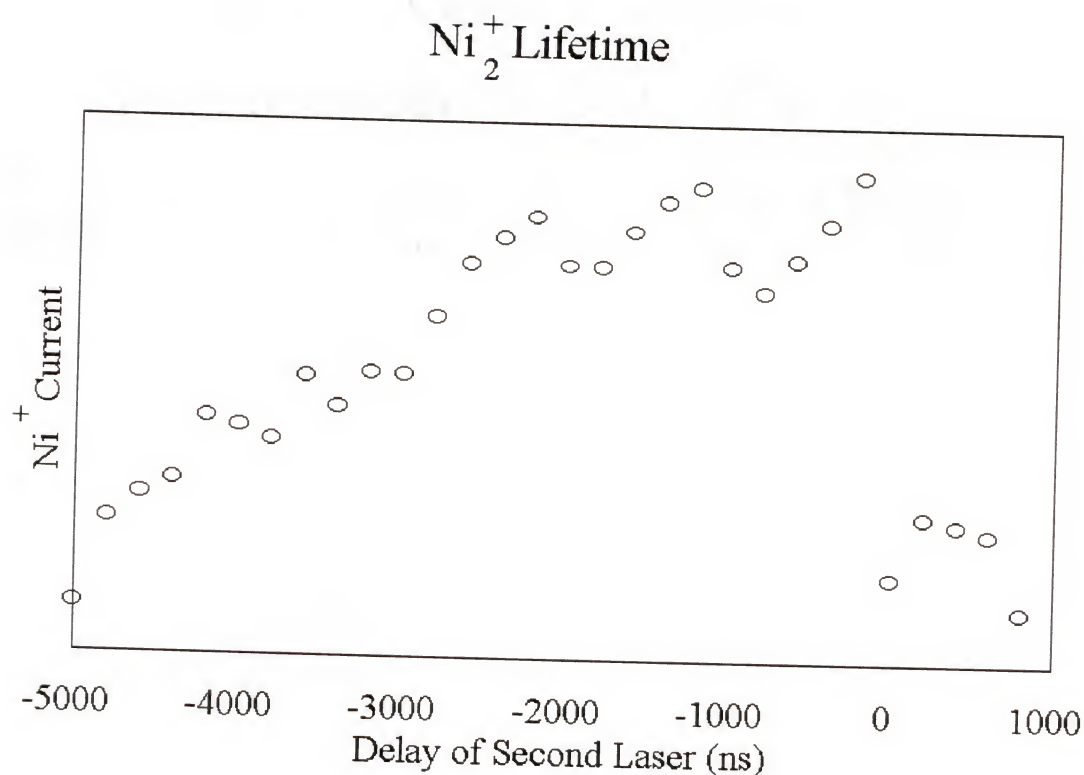


Figure 68. Attempted Ni_2^+ Lifetime Measurement.

The figure shows the curve obtained when the time between two laser pulses is varied for a two-color peak. The decay of the curve is directly related to the lifetime of the molecule. The Ni_2^+ molecule unfortunately undergoes a variety of decay relaxation mechanisms, which precludes exact determination of the upper state lifetime with this method.

complications due to relaxations steps which can not be determined in the current apparatus. Perhaps a high power picosecond laser would help elucidate the matter.

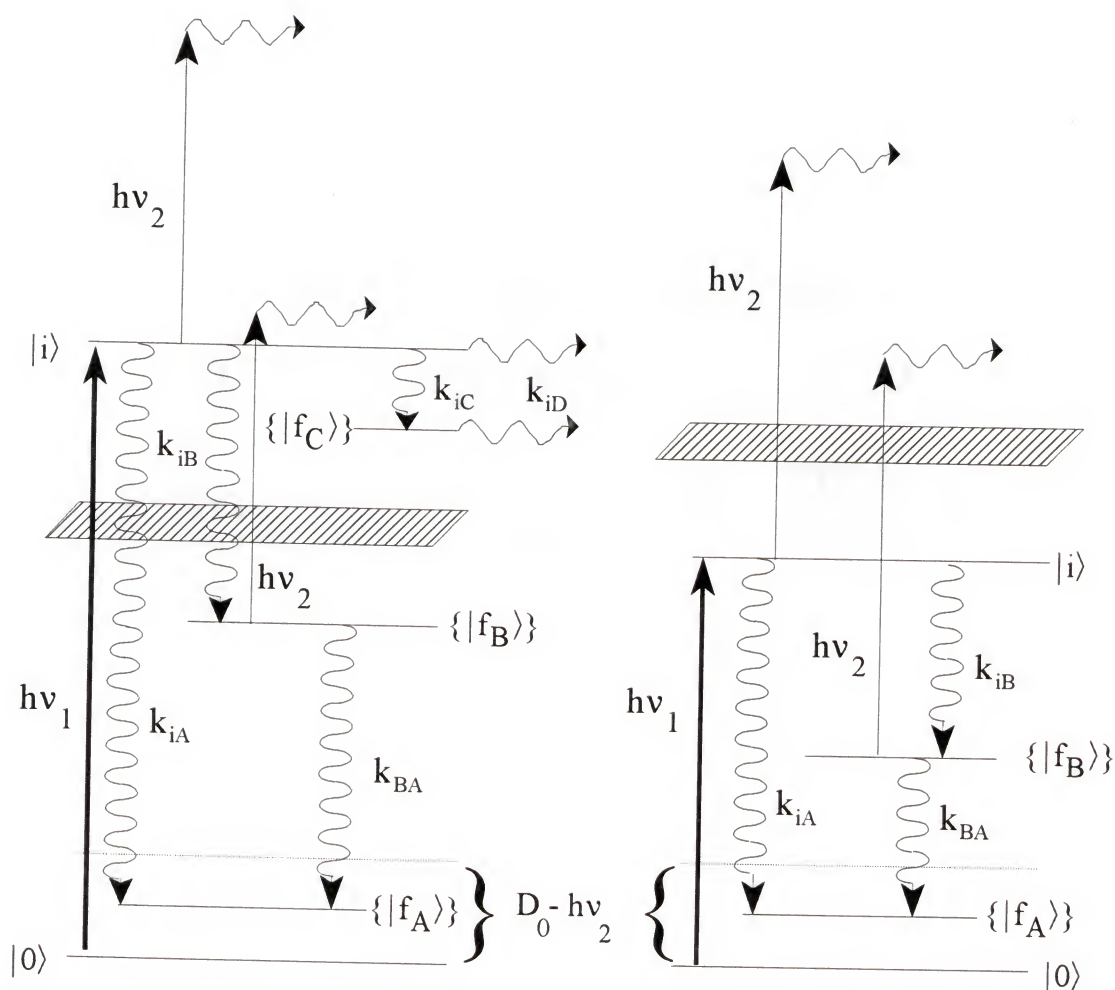


Figure 69. Possible Ni_2^+ Two-color Cascade Mechanisms.

The figure shows two possible cascade mechanisms for the two-color Ni_2^+ photodissociation process. The difference between the two is that the first photon is resonant and above the dissociation limit in the left panel and resonant and below the dissociation limit in the right. This cascade mechanism may explain the difficulty in measuring the lifetime of Ni_2^+ .

CHAPTER 6

SIMULATED ANNEALING

Molecular systems which contain only weak interatomic forces can model ion solvation. Small clusters of a transition-metal-ion and rare gas atoms provide a simplified and tractable collection of atoms where many of the complicating forces have all but been removed. These systems allow a detailed study of "floppy" molecules and the meaning of their conformations.⁵¹ The use of clusters as models for solvent interactions is not new.^{52,53} This section introduces Simulated Annealing (SA); following sections show how it works, how it has been applied to explore the global minima structures for $(M^+)Rg_n$ and how constrained simulated annealing is useful.

Simulated annealing is a very convenient method for determining a global minimum on a surface with many local minima. Kirkpatrick et al.⁵⁴ first applied this method to discrete combinatorial optimization problems. Vanderbilt and Louie⁵⁵ extended the method to problems with continuous variables. The method of SA was first applied to atomic clusters by Wille⁵⁶. More recently, Navon⁵⁷ et al. applied the method to mixed rare-gas clusters. The SA method is merely an extension of the Metropolis⁵⁸ Monte-Carlo algorithm.

Consider a function like $V(\mathbf{r})$ to be minimized for $\mathbf{r}=(r_1, r_2, \dots, r_n)$ defined in an n -dimensional space. The Metropolis Monte Carlo algorithm starts by choosing an initial

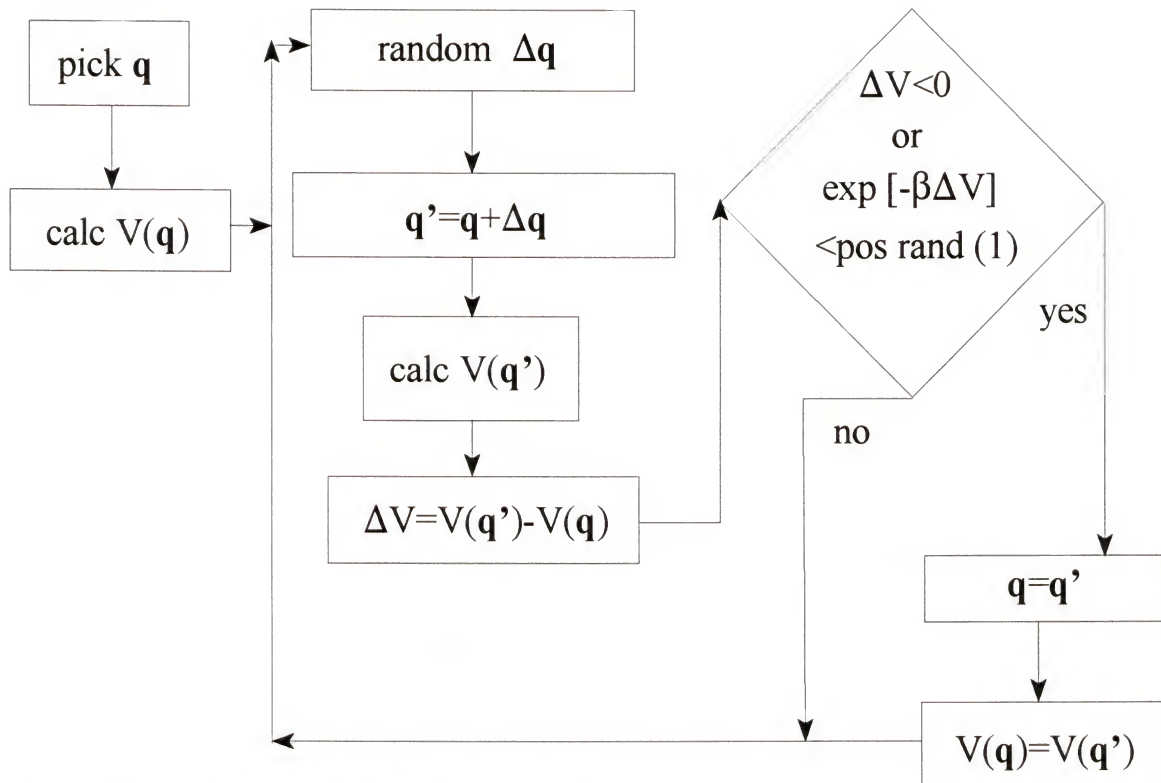


Figure 70. The Simulated Annealing Flow Diagram.

The figure shows the main flow of the SA algorithm. Basically the routine continues picking new configurations until no moves are made which change the potential by some criterion.

conformation $\mathbf{r}_0$ and then makes random moves $\Delta\mathbf{r}_i$. After each step, ΔV is calculated from $V(\mathbf{r}+\Delta\mathbf{r}) - V(\mathbf{r})$. If ΔV is negative the step is accepted; otherwise, it is accepted with some probability $\exp[-\beta(\Delta V)]$. The step size $\Delta\mathbf{r}$ is chosen such that the ratio of accepted to rejected steps is about 50%. If the annealing, done by raising β , is carried out slowly, the system will avoid being trapped in shallow local minima. The pseudotemperature controls the values of V that are acceptable. Lowering β allows the system to jump among local minima; raising β forces it to remain at a low minimum. This change of β represents an annealing process and this process must be repeated several times to assure that the global minimum has been found.

Informational Theoretical Approach

A treatment of SA similar to the one in thermodynamics but for these finite systems has been developed. This was accomplished using concepts of information theory.⁵⁹ The Hamiltonian (H) for these clusters is taken to be the classical kinetic (K) plus potential (V) energy

$$H(\mathbf{p},\mathbf{r}) = K(\mathbf{p}) + V(\mathbf{r}) \quad (26)$$

where $\mathbf{p}$ is the set of momenta $\{\mathbf{p}_i\}$ in Cartesian coordinates for all atoms i , and $\mathbf{r}$ is the set of Cartesian coordinates $\{\mathbf{r}_i\}$. The standard definition of missing information, I ,

$$I = -k \int d\mathbf{p} d\mathbf{r} P(\mathbf{p},\mathbf{r}) \ln P(\mathbf{p},\mathbf{r}) \quad (27)$$

where k is a dimensionality constant and $P(\mathbf{p}, \mathbf{r})$ is the probability that the system will be in state $(\mathbf{p}, \mathbf{r})$, is employed to describe a cluster or system of particles. I is maximized subject to the following constraints:

$$k \int d\mathbf{p} d\mathbf{r} P(\mathbf{p}, \mathbf{r}) = 1, \quad (28)$$

$$k \int d\mathbf{p} d\mathbf{r} P(\mathbf{p}, \mathbf{q}) R^{(\alpha)}(\mathbf{p}, \mathbf{q}) = \langle R^{(\alpha)}(\mathbf{p}, \mathbf{q}) \rangle \quad (29)$$

with $R^{(\alpha)}(\mathbf{p}, \mathbf{r})$ being some property of the system. Introducing the Lagrangian multipliers κ and λ_α , it is required that

$$I' [P(\mathbf{p}, \mathbf{r}), \kappa, \lambda_\alpha] = -k \int d\mathbf{p} d\mathbf{r} P(\mathbf{p}, \mathbf{r}) \ln P(\mathbf{p}, \mathbf{r}) + \kappa(\kappa+1)k \int d\mathbf{p} d\mathbf{r} P(\mathbf{p}, \mathbf{r}) + \sum_\alpha \lambda_\alpha k \int d\mathbf{p} d\mathbf{r} P(\mathbf{p}, \mathbf{r})^{(\alpha)} = \max, \quad (30)$$

and therefore for all $(\mathbf{p}, \mathbf{r})$

$$\frac{\partial I'}{\partial \kappa} = \frac{\partial I'}{\partial \lambda_\alpha} = \frac{\delta I'}{\delta P(\mathbf{p}, \mathbf{r})} = 0. \quad (31)$$

In the canonical ensemble $\lambda_1 = \beta$ (the pseudoinverse temperature) and $R^{(1)}(\mathbf{p}, \mathbf{r}) = H(\mathbf{p}, \mathbf{r})$ so that

$$\kappa = -\ln(k \int dp d\mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})}) = -\ln \Omega, \quad (32)$$

where Ω is the partition function. The probability is now

$$P(\mathbf{p}, \mathbf{r}) = e^{\kappa - \beta H(\mathbf{p}, \mathbf{r})}. \quad (33)$$

The pseudointernal energy of the cluster will be given by

$$\frac{\partial \kappa}{\partial \beta} = -\frac{\partial \ln \Omega}{\partial \beta} = \langle H \rangle = U, \quad (34)$$

while the average value of any property R of the system is given by

$$\langle R \rangle = \frac{\int dp d\mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})} R(\mathbf{p}, \mathbf{r})}{\int dp d\mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})}} \quad (35)$$

In particular, the average value of the potential energy is just

$$\langle V \rangle = \frac{\int d\mathbf{r} e^{-\beta V(\mathbf{q})} V(\mathbf{q})}{\int d\mathbf{r} e^{-\beta V(\mathbf{q})}} \quad (36)$$

since V is not a function of $\mathbf{p}$. The average kinetic energy with respect to a space-fixed

reference frame is a function of the pseudoinverse temperature given by

$$\langle K \rangle = \frac{3N}{2\beta}, \quad (37)$$

and the pseudointernal energy will be the sum of the two averages or just the average of the Hamiltonian, $U = \langle K \rangle + \langle V \rangle = \langle H \rangle$.

A pseudoheat capacity of the system may be defined as

$$C = \beta^2 \frac{\partial^2 \kappa}{\partial^2 \beta}, \quad (38)$$

which yields a simple expression

$$C = \beta^2 (\langle H^2 \rangle - \langle H \rangle^2). \quad (39)$$

Now as $\beta \rightarrow \infty$, or as the pseudotemperature goes to zero, we have $|\langle K^2 \rangle| \ll |\langle V^2 \rangle|$ and $|\langle K \rangle| \ll |\langle V \rangle|$. This means that the internal energy approaches the equilibrium potential energy $U \approx V_{eq}$ and that the heat capacity goes to zero, $C \approx 0$.

Calculation of Equilibrium Properties

Equilibrium properties can be obtained for $\beta \rightarrow \infty$, that is, for a pseudotemperature of 0.0K. For this β , one can immediately go about calculating the moment of inertia, dipole moment, and quadrupole moment of the clusters at their potential-energy global minimum. The components of the moment of inertia tensor are simply

$$(I)_{\xi\eta} = m_+ [\delta_{\xi\eta}(r_+)^2 - (r_+)_\xi(r_+)_\eta] + \sum_{i=1}^n m_i [\delta_{\xi\eta}(r_i)^2 - (r_i)_\xi(r_i)_\eta] \quad (40)$$

where $\mathbf{r}_i$ and $\mathbf{r}_+$ are used to indicate positions of Ar atoms and the metal ion in center-of-mass coordinates, with $\xi, \eta = x, y, z$ components of these vectors and $r^2 = x^2 + y^2 + z^2$ (see, for example, Marion⁶⁰).

The dipole moment of the cluster can be calculated in the center-of-charge (COC) coordinates by the sum of all of the induced dipoles as in Hirschfelder, et. al.²⁸

$$\mathbf{D}^{COC} = \alpha q_+ \sum_{i=1}^n \frac{\mathbf{R}_i}{R_i^3}, \quad (41)$$

where R_i is the distance from the i th Ar atom to the ion, α is the polarizability of the Ar, and q_+ is the charge on the ion. Alternatively, the dipole moment in center-of-mass (COM) coordinates can be given as

$$\mathbf{D}^{COM} = \sum_{i=1}^n q_i^- \mathbf{r}_i^- + \sum_{i=1}^n q_i^+ \mathbf{r}_i^+ = q_+ \mathbf{r}_+, \quad (42)$$

where

$$q_i^\pm \equiv \pm \frac{\alpha q_+}{2r_{Ar} R_i^2} \quad (43)$$

are charges induced at the Ar and $2r_{Ar}$ is the distance between fictitious charges in the induced dipole are given by

$$\mathbf{r}_i^\pm = \mathbf{r}_i \pm \frac{r_{Ar} \mathbf{R}_i}{R_i}. \quad (44)$$

The COM dipole moment reduces to a simple form

$$D^{COM} = q_+ (r_+ + \alpha \sum_{i=1}^n \frac{R_i}{R_i^3}), \quad (45)$$

which is the COC dipole plus the displacement of the ion from the COM of the cluster.

The COC quadrupole moment tensor is given by

$$Q_{\xi\eta}^{COC} = \sum_{i=1}^n q_i^+ [3(R_i^+)_{\xi}(R_i^+)_{\eta} - (R_i^+)^2 \delta_{\xi\eta}] + \sum_{i=1}^n q_i^- [3(R_i^-)_{\xi}(R_i^-)_{\eta} - (R_i^-)^2 \delta_{\xi\eta}], \quad (46)$$

where

$$R_i^{\pm} = R_i (1 \pm \frac{r_{Ar}}{R_i}) \quad (47)$$

are the positions of the charges of the induced dipoles. The COM quadrupole moment

can be derived from

$$Q_{\xi\eta}^{COM} = q_+ [3(r_+)_{\xi}(r_+)_{\eta} - (r_+)^2 \delta_{\xi\eta}] + \sum_{i=1}^n q_i^+ [3(r_i^+)_{\xi}(r_i^+)_{\eta} - (r_i^+)^2 \delta_{\xi\eta}] + \sum_{i=1}^n q_i^- [3(r_i^-)_{\xi}(r_i^-)_{\eta} - (r_i^-)^2 \delta_{\xi\eta}] \quad (48)$$

and from Eqs. (43) and (44) leading to

$$Q_{\xi\eta}^{COM} = q_+ \left[3(\mathbf{r}_+)_\xi (\mathbf{r}_+)_\eta - (\mathbf{r}_+)^2 \delta_{\xi\eta} \right] + \frac{\alpha q_+}{2r_{Ar}} \sum_{i=1}^n \left\{ 3 \left[\left(\mathbf{r} + \frac{r_{Ar} \mathbf{R}_i}{R_i} \right)_\xi \left(\mathbf{r} + \frac{r_{Ar} \mathbf{R}_i}{R_i} \right)_\eta - \left(\mathbf{r}_i - \frac{r_{Ar} \mathbf{R}_i}{R_i} \right)_\xi \left(\mathbf{r}_i - \frac{r_{Ar} \mathbf{R}_i}{R_i} \right)_\eta \right] - \frac{4r_{Ar} (\frac{\mathbf{r}_i \cdot \mathbf{R}_i}{r_i}) \delta_{\xi\eta}}{R_i^2} \right\} \quad (49)$$

which simplifies to give

$$Q_{\xi\eta}^{COM} = q_+ (3(\mathbf{r}_+)_\xi (\mathbf{r}_+)_\eta - \mathbf{r}^2 + \delta_{\xi\eta}) + \alpha q_+ \sum_{i=1}^n \left(\frac{\left\{ 3 \left[(\mathbf{r}_I)_\xi \left(\frac{\mathbf{R}_I}{r_I} \right)_\eta + (\mathbf{r}_I)_\eta \left(\frac{\mathbf{R}_I}{r_I} \right)_\xi \right] - 2\delta_{\xi\eta} \left(\frac{\mathbf{r}_i \cdot \mathbf{R}_i}{R_i} \right) \right\}}{R_i^2} \right). \quad (50)$$

The arbitrary coordinate system chosen at the start of the calculation is transformed by rotation into the principal moment of inertia frame. In this frame, the moment of inertia tensor is diagonal with three unique elements I_a, I_b , and I_c which are related to the rotational constants A, B , and C by $A = h / 8\pi^2 c I_a$ etc., where h and c are Planck's constant and the speed of light, respectively, and $I_a \leq I_b \leq I_c$ as is the usual ordering (see Steinfeld⁶¹). The COM electric dipole and quadrupole moments are also calculated in this frame.

The moment of inertia tensor is symmetric and is easily diagonalized by a rotation from the space-fixed reference frame to the body-fixed reference frame, to obtain the principal moments of inertia. The dipole vectors and quadrupole tensors can similarly be transformed to the principal moments frame.

Table XV. Potential Parameters for I to IV and I + dd to IV + dd.

Metal-Rare-Gas Interaction Parameters							
Potential	D _e (eV)	D _M (eV)	R _e (Å)	ω _e (cm ⁻¹)	R _s (Å)	a (Å ⁻¹)	a _s (Å ⁻¹)
i ^a	0.524	0.5104	1.84	238	2.760	1.978	3.956
ii ^a	0.381	0.3708	1.99	193	2.980	1.820	3.640
iii ^b	0.403	0.4032	2.43	177	3.909	1.840	3.680
iv ^b	0.299	0.2992	2.64	143	4.364	1.679	3.358
Argon-Argon Interaction Parameters ^c							
C ₆ [*]	-1.180			b ₀	-0.7		
C ₈ [*]	-0.6118			b ₁	1.8337		
C ₁₀ [*]	0			b ₂	-4.5740		
x ₀	1.1263			b ₃	4.3667		
x ₁	1.4000			γ	6.279		
D _e	0.0127 eV			R _e	3.760 Å		
Dipole-Dipole Interaction Parameters							
R _c	2.00 Å		b _c	2.00 Å ⁻¹		α _{Ar}	1.66 Å

^a D_e , R_e and ω_e taken from references 8 and 13.

^b D_e , R_e and ω_e taken from reference 62.

^cAll values taken from reference 64.

Construction of the Many-Atom Potential

The total potential energy for a $(M^+)L_n$ cluster is assumed to be a sum of two-atom and three-atom interactions,

$$V = \sum_{1 \leq i \leq n} V_{M^+L_i} + \sum_{1 \leq i < j \leq n} V_{L_iL_j} + \sum_{1 \leq i < j \leq n} V_{M^+L_iL_j} \quad (51)$$

The first term is the potential due to the charged metal ion interacting with the rare gas L_i . The second, two-atom, term is the interaction of two rare gas atoms L_i and L_j , and the three-atom term contains the interaction of the rare-gas atomic dipoles induced by the metal ion. Other interactions in the multiple expansion have not been included but are assumed to be small in comparison with the terms above.

The M^+ -L Potential

The properties of first-row transition-metal ions complexed to a single Ar atom have been investigated previously both experimentally^{8,13} and by *ab initio* theory.⁶² Experimental results confirm the behavior of the long-range potential as $1/R^4$ and provide very accurate well depths, D_e , for the ground-state surface. Theory has provided dissociation energies, vibrational frequencies, ω_e , and equilibrium internuclear distances, R_e , for the ground state. Theory systematically underestimates the dissociation energy of the molecules by ca.20%. Experimenters⁵ have estimated ω_e and R_e for ground states by inference from excited-state properties. Again, theory systematically overestimates equilibrium bond lengths and underestimates vibrational frequencies. Four sets of parameters have been chosen for $\{D_e, R_e, \omega_e\}$ that are presently available from the experimenters' and theorists' determinations of the properties of $CoAr^+$ and VAr^+ . These parameters are listed in Table XV, for potentials labeled (i), (ii), and (iv), chosen in order of increasing ionic radii. Potentials (i) and (ii) are parametrized expressions from experiments for Co^+ and V^+ , while (iii) and (iv) are parametrized expressions from theory for Co^+ and V^+ , respectively.

M^+ - Ar Potentials

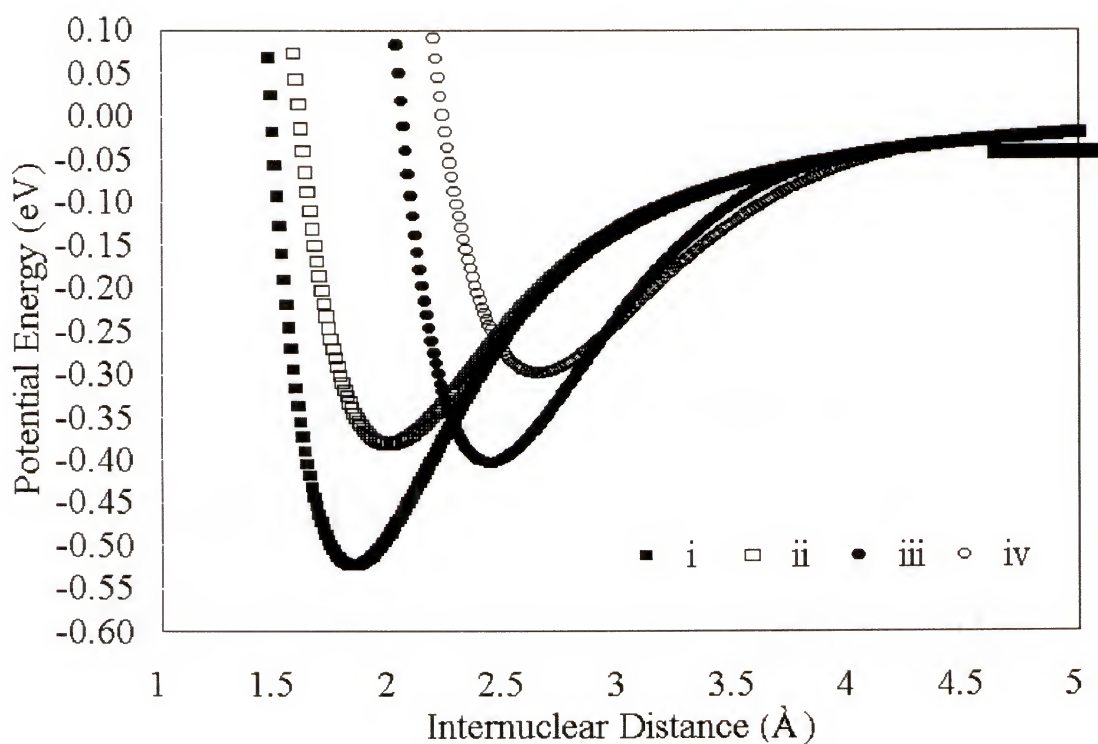


Figure 71. Potentials i, ii, iii and iv for the M^+ -Ar Interaction.

The figure shows a plot of the four parameterizations of the MS4 potential. (i) and (ii) represent a potential which fits experimental parameters for Co^+ and V^+ interacting with Ar respectively. (iii) and (iv) represent the MS4 potential with theoretical parameters for Co^+ and V^+ interacting with Ar respectively.

Ar-Ar pair potential

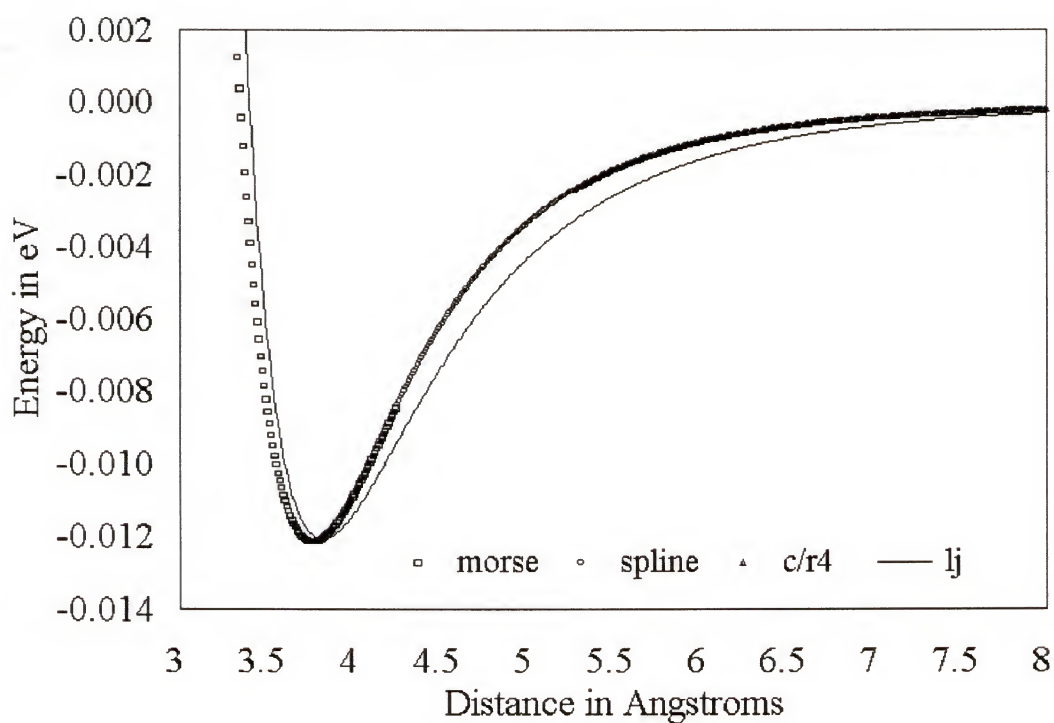


Figure 72. MSVIII and LJ12-6 Ar-Ar Potential.

The figure shows a comparison of the relatively simple Lennard-Jones 12-6 potential and the MSVIII potential. They are very similar, however the MSVIII is more realistic for the short range behavior and the binding energy.

A fit to a modified Morse potential with the following form has been employed for the above (D_e , R_e , ω_e) parameters:

$$V_{M^+L}(R) = [1 - f_s(R)]V_M(R) + f_s(R)V_4(R), \quad (52)$$

where V_M is the usual Morse potential

$$V_M(R) = D_M[e^{-2a(R-R_e)} - 2e^{-a(R-R_e)}], \quad (53)$$

and V_4 is the charge-induced dipole potential

$$V_4(R) = \frac{-\alpha q^2}{2R^4} \quad (54)$$

The asymptotic form of this potential is given by the literature value⁶³ of the polarizability⁵³ of Ar, $\alpha=1.66\text{\AA}^3$. The switching function $f_s(R)$ between the Morse potential and the long-range asymptotic form was chosen as

$$f_s(R) = [1 + e^{-a_s(R-R_s)}]^{-1}, \quad (55)$$

where R_s is the point at which switching is done and a_s determines the range of the switching. The values of the constants in Eqs. (53) and (55) chosen to fit $\{D_e, R_e, \omega_e\}$ are also found in Table XV. This is referred to as the Morse-switch-4 (MS4) potential. The various parametrizations for the MS4 potentials (i)-(iv) are displayed graphically in Figure 71.

The Ar-Ar Potential

The crossed-beam studies by Parson, Lee, and Siska⁶⁴ have given the Ar-Ar potential, broken into three regions, as a Morse potential joined to the long-range van der Waals interaction by a spline function,

$$V^*(R^*) = e^{-2\gamma(R^*-1)} - 2e^{-\gamma(R^*-1)}, \quad R^* < x_0, \quad (56)$$

$$V^*(R^*) = b_0 + (R^* - x_0) \left\{ b_1 + (R^* - x_1) \right\} \left[b_2 + (R^* - x_1) b_3 \right], \quad x_0 < R^* \leq x_1, \quad (57)$$

$$V^*(R^*) = \frac{C_6^*}{R^{*6}} - \frac{C_8^*}{R^{*8}} - \frac{C_{10}^*}{R^{*10}}, \quad x_1 < R^*, \quad (58)$$

where the reduced quantities are given by

$$R^* = R/R_e, \quad (59)$$

$$V^*(R^*) = V(R^*)/D_e, \quad (60)$$

$$C_n^* = C_n / (D_e R_e^n). \quad (61)$$

The constants for what they call the MSVIII potential are also included in Table XV.

Interaction of Charge-Induced Dipoles

The potential for the interaction of two charge-induced dipoles, a three-atom potential, is given by

$$V_{M^+L_iL_j}(\mathbf{R}_i, \mathbf{R}_j) = \frac{q_+^2 \alpha_i \alpha_j}{(R R_i R_j)^3} \left\{ (\mathbf{R}_i \cdot \mathbf{R}_j) - \frac{3(\mathbf{R}_i \cdot \mathbf{R})(\mathbf{R}_j \cdot \mathbf{R})}{R^2} \right\} f_c(R), \quad (62)$$

where R_i is the magnitude of the vector from the ion to L_i , R is the magnitude of the vector between L_i and L_j , α_i is the polarizability of L_i , and q_+ is the charge of the metal ion M^+ . The potential is cut off at short distances to avoid unrealistic behavior, with the function

$$f_c(R) = (1 + e^{-b_c(R-R_c)})^{-1}, \quad (63)$$

where R_c is the cutoff distance and b_c governs the width of the cutoff.

This cutoff function must be very carefully chosen to avoid cutting off the potential at what would be typical Ar-Ar distances in the clusters. R_c and b_c were varied systematically to ensure that no equilibrium properties or structures were affected by their values. The cutoff is rapid and occurs at a considerably smaller distance than typical Ar-Ar separations in these cluster ions. See Table XV, for chosen values R_c and b_c .

Simulated Annealing Algorithm

1. Start with an initial inverse pseudotemperature $\beta=1/(k_B T)$, and a chosen initial conformation $\mathbf{r}$. Choose an initial magnitude of $\Delta \mathbf{r}$ for the atom displacements (step size).

2. Calculate the potential energy for $\mathbf{r}$, $V(\mathbf{r})$.
3. Choose a new conformation $\mathbf{r}' = \mathbf{r} + \Delta\mathbf{r}$ by displacing an atom at a time and calculate the new potential energy of the system, $V(\mathbf{r}')$.
4. Calculate $\Delta V = V(\mathbf{r}') - V(\mathbf{r})$.
5. If $\Delta V < 0$ always accept the new conformation.
6. If $\Delta V > 0$ and $\exp(-\beta\Delta V)$ is smaller than a random number between 0 and 1 then accept the new conformation even though it is higher in energy; otherwise reject it.
7. If more than 50% of the attempted conformations are rejected, decrease the step size.
8. If the number of conformation changes reaches 1,000, increase β .
9. Repeat steps 3 through 8 and continue until β has reached $\beta_{\max}$ or until ΔV stays smaller than some tolerance τ .
10. Repeat the entire process to insure that the global minimum has been located.

Application of SA to CoAr_n^+ and VAr_n^+

The minimum potential-energy conformation of the MAr_n^+ cluster ions have been determined for eight different total potentials for $n = 1$ to 14. The results can be analyzed in terms of a fixed number of Ar atoms while varying the total potential or for a given potential with an increasing number of Ar atoms. It can also be read as a matrix of results where potentials are varied along rows and the number of Ar atoms is varied along columns.

Calculations for total potentials labeled I to IV are based upon the $M^+ \cdot Ar$ potential parameters labeled (i) to (iv) in Table XV, the Ar-Ar potential (also in Table XV) and no three body term. The configurations from these calculations have been tabulated in Table XVI. The configurations in Table XVII are for the analogous calculations which include the interaction of the ion-induced dipole forces (parameters are in Table XV) and are labeled I + dd to IV + dd.

The convenience of labeling the two sets of total potentials without and with the three body term to I to IV and I + dd to IV + dd, respectively, becomes more apparent if it is noted that the potential parameters and calculations are numbered corresponding to metal ions of increasing size. The results along rows may be interpreted as representing typical complexes of first row singly-charged transition-metal cations of increasing size from left to right. For a given potential, increasing the number of atoms n leads to the formation of solvation shells. These are made up of atoms located at the same distance from the central ion or within a narrow range of distances. As n is increased, the innermost solvation shell forms a core of argons strongly bound to the ion. Additional solvation atoms may simply cap faces of this shell, slightly distort it or even force it open and thereby increase the coordination of the central ion with the Ar atoms of the innermost shell. The core of solvation atoms often has a high or only slightly distorted symmetry. Table XVI and Table XVII reflect the symmetry of the innermost solvation shell. Structures with tetrahedral or near tetrahedral first shells are labeled **ctet**, for capped tetrahedra. Structures with octahedral or near octahedral first shells are labeled

coct. Structures with square antiprismatic first shells are labeled **csap**. These structures are displayed in **Figure 73**.

Understanding of the various structures listed in **Table XVI** and **Table XVII** can be gained by following the natural classification, based upon the inner solvation a little further. Additional solvation shells depend upon this core solvation shell because of their geometries. **Table XVIII** list three core geometries obtained with the eight total potentials according to the size of the innermost core structure. The tetrahedral core seems to occur as a global minimum for very small metal ions. This is seen in the range of first-shell distances from the ion. The octahedral core forms for somewhat larger ions, and the SAP core is found for the largest ions in this investigation. Though these are generalizations and the effective size is dependent upon the dd contribution, it is clear that a larger ion allows more argons in its innermost solvation shell.

? to ? display the total potential energy and each of the contributions to it for each of the potentials I through IV+dd. The figures on the left hand side were obtained when no dd term was included. The figures on the left were obtained when the dd term was included. Each figure is labeled I to IV+dd. Additionally, the total binding energy has been labeled with hollow squares, the dd term by filled triangles, the Ar-Ar interaction by hollow triangles and the M^{+} -Ar interaction by filled squares. The total binding energies have been placed in ? as well. What is clear from the figures and the table is that the total binding energy goes up as argon atoms are added. The amount which the binding energy goes up seems to level off after a point, as would be expected.

Table XVI. Configurations and Symmetries for $M^+ \cdot Ar_n$ for Potentials I thru IV.

n	I	II	III	IV
1	Linear $C_{\infty v}$	Linear $C_{\infty v}$	Linear $C_{\infty v}$	Linear $C_{\infty v}$
2	Linear $D_{\infty h}$	Bent C_{2v}	Bent C_{2v}	Bent C_{2v}
3	Trigonal planar D_{3h}	Trigonal planar D_{3h}	Pyramidal C_{3v}	Pyramidal C_{3v}
4	Tetrahedral T_d	Tetrahedral T_d	Tetrahedral T_d	Seesaw C_{2v}
5	ctet C_{3v}	ctet C_{3v}	Square pyramidal C_{4v}	Square pyramidal C_{4v}
6	ctet C_{2v}	Octahedral O_h	Octahedral O_h	Octahedral O_h
7	ctet C_{3v}	coct C_{3v}	coct C_{3v}	7-coordinate C_{2v}
8	ctet T_d	coct C_{2v}	Square antiprism S_8	Square antiprism S_8
9	ctet	coct	csap C_{4v}	csap C_{4v}
10	ctet	coct	csap S_8	csap S_8
11	ctet	ctet	csap C_{2v}	csap C_{2v}
12	ctet	ctet	csap	csap
13	ctet	ctet C_{3v}	csap	csap
14	ctet	ctet T_d	csap	csap

Table XVII. Configurations and Symmetries for $M^+ \cdot Ar_n$ for Potentials I + dd thru IV + dd.

n	I + dd	II + dd	III + dd	IV + dd
1	Linear $C_{\infty v}$	Linear $C_{\infty v}$	Linear $C_{\infty v}$	Linear $C_{\infty v}$
2	Linear $D_{\infty h}$	Linear $D_{\infty h}$	Linear $D_{\infty h}$	Linear $D_{\infty h}$
3	Trigonal planar D_{3h}	Trigonal planar D_{3h}	Trigonal planar C_{3v}	T-shaped C_{3v}
4	Tetrahedral T_d	Tetrahedral T_d	Tetrahedral T_d	Distorted tet C_{2v}
5	ctet C_{3v}	ctet C_{3v}	Square pyramidal C_{4v}	Square pyramidal C_{4v}
6	ctet C_{2v}	ctet C_{2v}	Octahedral O_h	Octahedral O_h
7	ctet	ctet C_{3v}	coct C_{3v}	7-coordinate
8	ctet	ctet	coct C_{2v}	Square antiprism S_8
9	ctet	ctet	coct C_s	csap C_{4v}
10	ctet	ctet	coct	csap
11	ctet	ctet	coct	csap
12	ctet	ctet	coct	csap
13	ctet	ctet	coct	csap
14	ctet	ctet	coct	csap

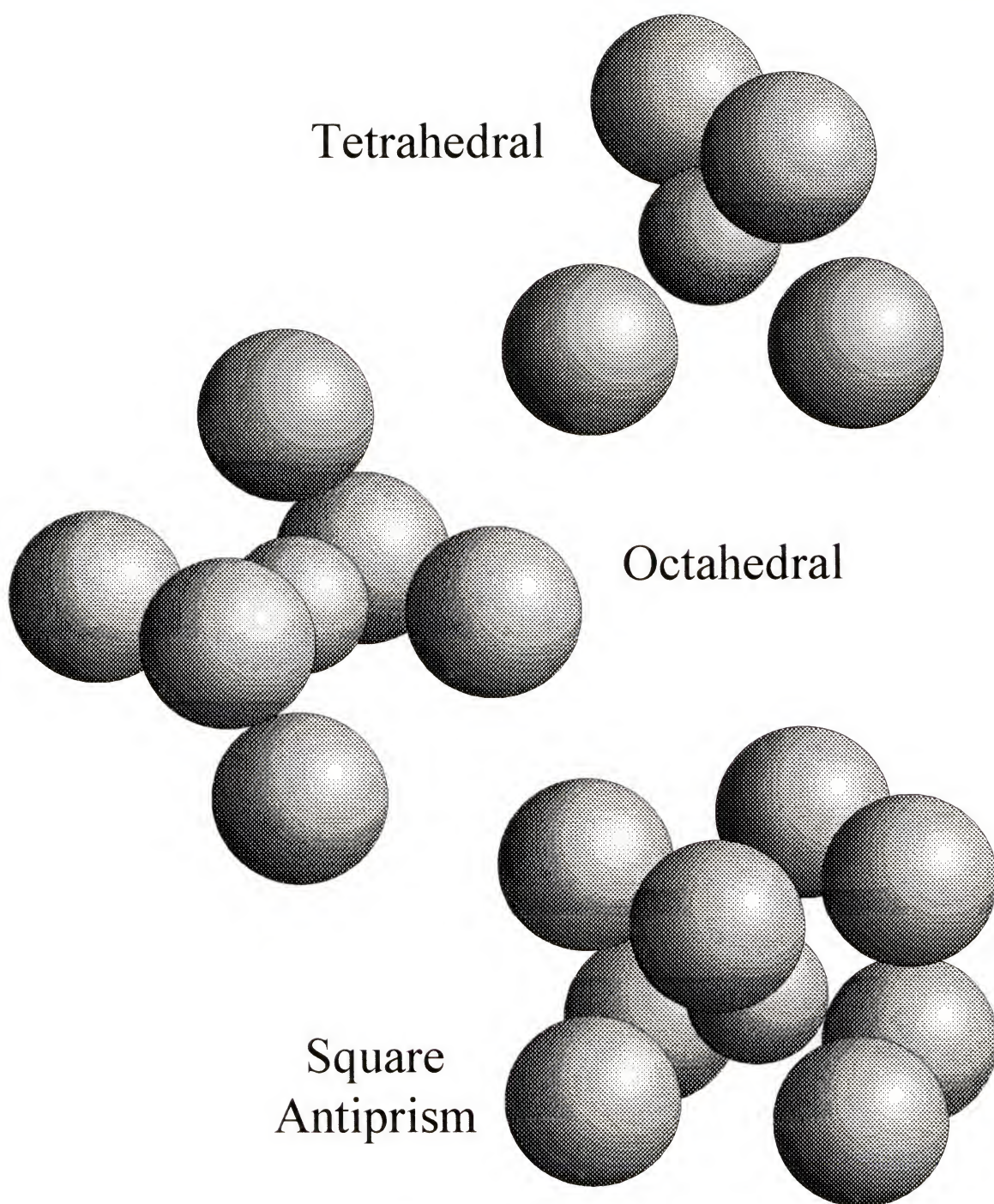


Figure 73. Three Solvation Cores **tet**, **oct** and **sap**.

The upper right figure shows the smallest solvation core of VAr_n^+ , the tetrahedral configuration. The middle shows the familiar octahedral configuration. The lower right is the largest, the square antiprism. The abbreviations **ctet**, **coct** and **csap** are used widely in the text to describe capped structures based upon these central cores.

Table XVIII. Shell Properties for Three Core Structures.

Core Structure	Shell Number	Shell Geometry	Shell radius (Å)	Maximum Occupation
Tetrahedral	1	Tetrahedral	1.97-2.22	4
	2	Tetrahedral	3.65-3.83	4
	3	Octahedral	4.30-4.51	6
Octahedral	1	Octahedral	2.47-2.71	6
	2	Cubic	4.39-5.10	8
Square antiprism	1	Square Antiprism	2.64-2.85	8
	2	Distorted Octahedral	4.22-5.20	6

The total binding energy $E_n = -\min(V_n)$ for each cluster. In ? through ? we can see graphically what the geometry tables were telling us. As the core solvation shells are closed, there is a significant drop in binding energy per argon. This happens again for the second solvation shell, but to a lesser extent. Comparing two panels with and without the dd term, it is clear that the dd term in general lowers the total binding energy and that the sum of dd terms is always repulsive.

? and ? of I and I+dd show that the smallest ions modeled, with or without the three-body term, rapidly form a tetrahedral core and then use this as the basis for further solvation shells. ? is a good example of the tetrahedral core forming early on and then switching to octahedral to accommodate more argons at high binding energy per argon.

In γ the tetrahedral core remains as the dd term repels the argons away from each other and no longer allows the octahedral configuration. γ shows a monotonic decrease in potential until the octahedral structure is formed. This octahedral structure is then capped a single argon and addition of a second causes rearrangement into a SAP core. γ shows similar behavior except the octahedral configuration is preferred throughout. Potential IV and IV+dd are the largest ions of all both γ and γ go through nearly the same core arrangements.

The equilibrium properties have been calculated from the $\beta \rightarrow \infty$ simulations. Reported here are the properties of the structures corresponding to potentials parameterized from the experimental values, namely I and II, with the inclusion of the dd term. The moment of inertia tensor has been diagonalized via a rotation from the space-fixed frame to a body-fixed frame to obtain principal moments of inertia, and these have been inverted to give the rotational constants in cm^{-1} , listed in Table XIX. These values are similar for the Co and V clusters, decreasing in general as n increases due to the larger moments of inertia. This table allows each cluster to be classified as spherical tops with $A=B=C$, as found in the MAr_4^+ , prolate or oblate symmetric tops with $A=B \neq C$ and asymmetric tops with $A \neq B \neq C$.

The COM dipoles and quadrupoles have also been rotated into the space-fixed frame and are reported in esu (10^{-18} esu = 1 D, so that water has a dipole of 1.84 D). The COM dipole vector components and their vector magnitudes have been listed in Table XX. Since the principal moments of inertia frame does not define the sign ($\pm$) of the dipole, the a-axis direction is chosen to give a positive D_a . Many of the small clusters

Table XIX. Equilibrium Rotational Constants for I + dd and II + dd.

n	Co ⁺ ·Ar _n Rotational Constants			V ⁺ ·Ar _n Rotational Constants		
	cm ⁻¹ × 10 ⁻³			cm ⁻¹ × 10 ⁻³		
	A	B	C	A	B	C
1	-	209	209	-	190	190
2	-	58	58	-	51	51
3	69	69	35	62	62	31
4	35	35	35	32	32	32
5	35	17	17	32	17	17
6	22	13	11	20	12	9.5
7	17	8.4	8.0	12	12	8.1
8	11	8.4	6.2	15	5.7	5.7
9	8.9	6.9	5.3	6.9	6.1	5.3
10	8.0	4.5	4.5	8.1	4.5	4.5
11	6.1	4.4	3.8	4.8	4.8	4.5
12	4.7	4.5	3.9	4.7	4.4	3.9
13	4.4	3.2	3.1	4.6	3.4	3.1
14	4.3	2.9	2.4	3.6	3.1	2.7

(n=2 to 4) have small or zero dipole moments, indicating their high symmetry. Those which have dipole moments have it only on one axis. The larger clusters have somewhat larger dipole moments due to their lower symmetry and the displacement of the charge from the center of mass. As in the smaller clusters, several of the symmetric clusters have only a single nonzero component. The COM quadrupole tensor components are given in Table XXI for the I+dd and I+dd structures. The highly symmetric clusters have small off-diagonal tensor components, as expected in the body-fixed (or principal moments of inertia) frame.

Table XX. Dipole Moments for CoAr_n^+ and VAr_n^+ from Simulated Annealing.

n	CoAr_n^+ COM dipole in 10^{-18} esu				VAr_n^+ COM dipole in 10^{-18} esu			
	D_a	D_b	D_c	D	D_a	D_b	D_c	D
1	1.21	0.00	0.00	1.21	-2.18	0.00	0.00	2.18
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	2.31	0.00	0.00	2.31	2.33	0.00	0.00	2.33
6	0.00	-2.24	0.00	2.24	0.03	2.81	0.10	2.81
7	1.81	-1.72	-1.46	2.89	0.00	0.00	1.66	1.66
8	5.16	-2.01	0.38	5.55	0.00	-1.71	0.00	1.71
9	4.46	-3.49	-0.32	5.67	-2.29	-1.46	2.50	3.68
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	2.90	-1.67	-2.51	4.19	0.00	0.00	2.46	2.46
12	-7.01	-0.06	-1.47	7.16	7.32	0.04	-1.55	7.48
13	0.31	-3.70	5.16	6.36	3.33	-0.01	-3.78	5.03
14	-3.39	0.30	-2.44	4.19	-1.54	-3.43	-0.17	3.76

Table XXI. Quadrupole moment components for $\text{Co}^+\cdot\text{Ar}_n$ and $\text{V}^+\cdot\text{Ar}_n$.

n	$\text{Co}^+\cdot\text{Ar}_n$ (in 10^{-26} esu.) ⁱ					$\text{V}^+\cdot\text{Ar}_n$ (in 10^{-26} esu.) ⁱ				
	Q_{aa}	Q_{ab}	Q_{ac}	Q_{bb}	Q_{bc}	Q_{aa}	Q_{ab}	Q_{ac}	Q_{bb}	Q_{bc}
1	15.64	0.00	0.00	-7.82	0.00	16.33	0.00	0.00	-8.16	0.00
2	33.59	0.00	0.00	-16.79	0.00	31.30	0.00	0.00	-15.65	0.00
3	11.90	0.00	0.00	11.90	0.00	11.25	0.00	0.00	11.25	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	10.06	0.00	0.00	-5.03	0.00	9.84	0.00	0.00	-4.92	0.00
6	7.00	0.00	0.00	1.91	0.00	8.89	-0.44	1.17	1.62	-0.20
7	11.76	-3.44	-0.71	-3.94	2.81	3.37	0.00	0.00	3.37	0.00
8	19.45	-8.35	4.49	-1.87	-0.24	16.28	0.00	2.42	-6.12	0.00
9	15.38	-11.78	1.77	3.82	1.05	7.44	4.17	-4.23	-1.88	-3.37
10	14.87	0.00	0.00	-7.44	0.00	14.51	0.00	0.00	-7.25	0.00
11	11.42	-3.97	-7.46	-0.90	4.82	-1.06	0.00	0.00	-1.06	0.00
12	28.14	0.33	11.66	-9.61	0.10	29.65	0.20	-12.38	-10.53	-0.06
13	-2.15	-4.43	1.83	-4.60	-19.88	11.91	-0.10	-7.22	-8.68	0.03
14	21.15	0.55	10.12	-5.19	-0.18	5.94	3.76	1.61	5.10	0.28

ⁱThe value of Q_{cc} follows from $Q_{aa} + Q_{bb} + Q_{cc} = 0$.

Constrained Simulated Annealing

The constrained SA method is merely an extension to the previously demonstrated SA technique. It fixes a single distance and minimizes the potential energy allowing all other distances to change according to the following algorithm:

1. Start with an initial inverse pseudotemperature $\beta=1/(k_B T)$, a chosen initial conformation $\mathbf{r}$. Choose an initial magnitude of $\Delta\mathbf{r}$ for the atom displacements (step size), with the distance of the ion to one of the rare gas atoms fixed.
2. Calculate the potential energy for $\mathbf{r}$, $V(\mathbf{r})$.
3. Choose a new conformation $\mathbf{r}' = \mathbf{r} + \Delta\mathbf{r}$ by displacing one atom at a time and calculate the new potential energy of the system, $V(\mathbf{r}')$.
4. Calculate $\Delta V = V(\mathbf{r}') - V(\mathbf{r})$.
5. If $\Delta V < 0$ always accept the new conformation.
6. If $\Delta V > 0$ and $\exp(-\beta\Delta V)$ is smaller than a random number between 0 and 1 then accept the new conformation even though it is higher in energy; otherwise reject it.
7. If more than 50% of the attempted conformations are rejected, decrease the step size.
8. If the number of conformation changes reaches 1,000, increase β .
9. Repeat steps 3 through 8 and continue until β has reached $\beta_{\max}$ or until ΔV stays smaller than some tolerance τ .
10. Repeat the entire process to insure that the global minimum has been located.

11. Vary the fixed distance and repeat all steps above until a plot of potential energy versus constrained distance can be constructed.

Following the procedure above we obtain **Figure 74**, a plot which shows two intersecting curves. One curve has a minimum around the VAr_6^+ oct configuration and another around the ctet configuration. The intersection is actually a pseudo crossing V_{psc} since the values are only a projection on the plane of the reaction coordinate of the actual PES for a constrained distance.

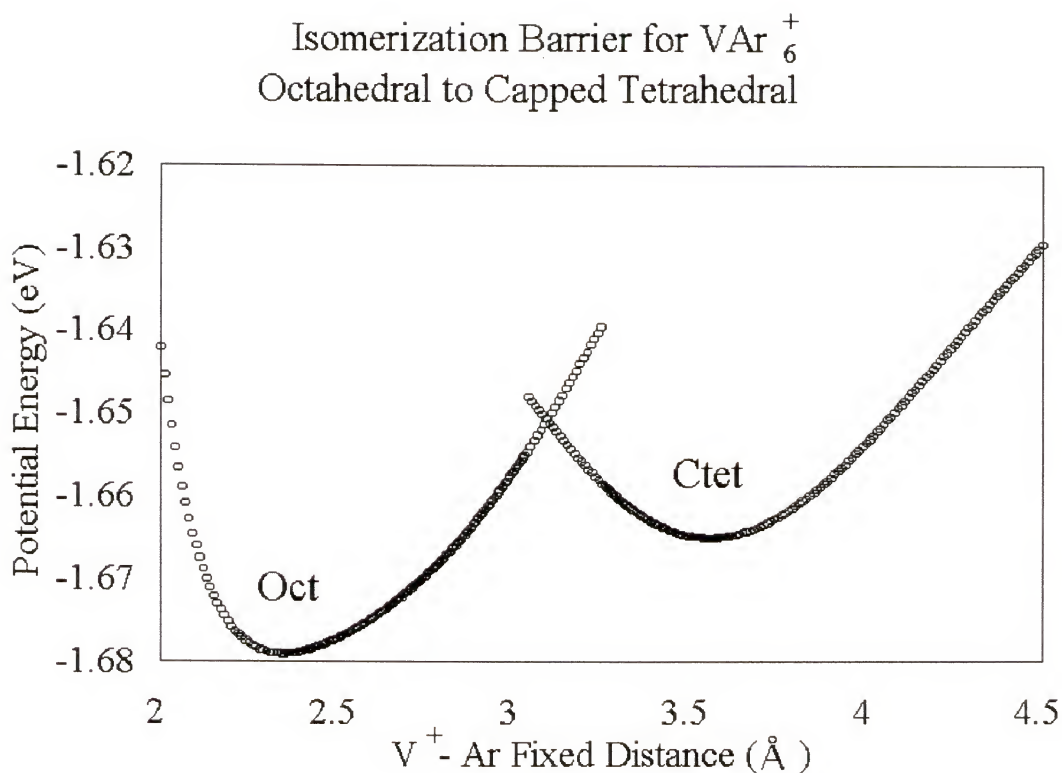


Figure 74. Pseudo Isomerization Barrier for VAr_6^+ .

The figure shows results from constrained SA and MD (explained in the following chapter) which yields two potential minima and a pseudocrossing at $r(V^+-Ar) = 3.08\text{\AA}$ and potential energy $V_{psc} = 0.02838\text{ eV}$ from the Oct conformation to the Ctet isomer. The distance between the V^+ and Ar pair has been fixed and energy minimized using the two methods at each distance.

CHAPTER 7 CLASSICAL TRAJECTORIES

Classical trajectories seem to be the next logical step after modeling the static properties of the clusters with simulated annealing. Dynamic modeling provides greater insight into these systems as they might exist in the experimental apparatus. The clusters in the experiment are not at zero Kelvin and therefore will have some ensemble properties. It can be argued that the cluster studied in the gas phase should be modeled as a microcanonical ensemble. However, a great deal of work has been done in high pressure mass spectrometers and in rare gas matrices, and these are clearly more like a canonical distribution.

The Hamiltonian for the cluster is taken to be the classical kinetic (K) plus potential (V) energy,

$$H(\{\mathbf{p}_i, \mathbf{r}_i\}) = K(\{\mathbf{p}_i\}) + V(\{\mathbf{r}_i\}) \quad (64)$$

where $\mathbf{p}_i$ and $\mathbf{r}_i$ are the momentum and position of atom i . The total kinetic energy is just the sum over all atoms i (with $i=0$ for V^+ and $i=1-n$ for the six Ar atoms)

$$K = \sum_{0 \leq i \leq n} \frac{|\mathbf{p}_i|^2}{2m_i} \quad (65)$$

while the total potential energy for the $M^+(L)_n$ cluster is assumed to be a sum of two-atom interactions

$$V = \sum_{1 \leq i \leq n} V_{M^+L_i} + \sum_{1 \leq i < j \leq n} V_{L_iL_j} \quad (66)$$

The first term in the potential is due to the charged metal ion interacting with a rare-gas atom. The second is the interaction of two rare-gas atoms. Work in the previous chapter had included other terms in the multipole expansion. These could be included here, but for the present studies the simplicity of the pair potentials is convenient for calculations and gives an adequate picture. The forces are calculated from the gradient of the potentials in the usual way,

$$\mathbf{F}_{ij} = -\nabla_{\mathbf{r}_{ij}}(V(\mathbf{r}_{ij})) \frac{\mathbf{r}_{ij}}{r_{ij}}. \quad (67)$$

Microcanonical and Canonical Cluster Dynamics

For a system at the phase space point $\Gamma(t) = [\mathbf{p}(t), \mathbf{r}(t)]$, with initial value Γ_0 at time t_0 , a property A can be expressed as

$$A[\mathbf{p}(t), \mathbf{r}(t)] = A[\Gamma(t; \Gamma_0)] \quad (68)$$

the average value of which is

$$\langle A(t) \rangle_f = \int d\Gamma_0 A(\Gamma(t; \Gamma_0)) f(\Gamma_0) \quad (69)$$

VAr_n^+ Capped Tetrahedral Radial Distributions

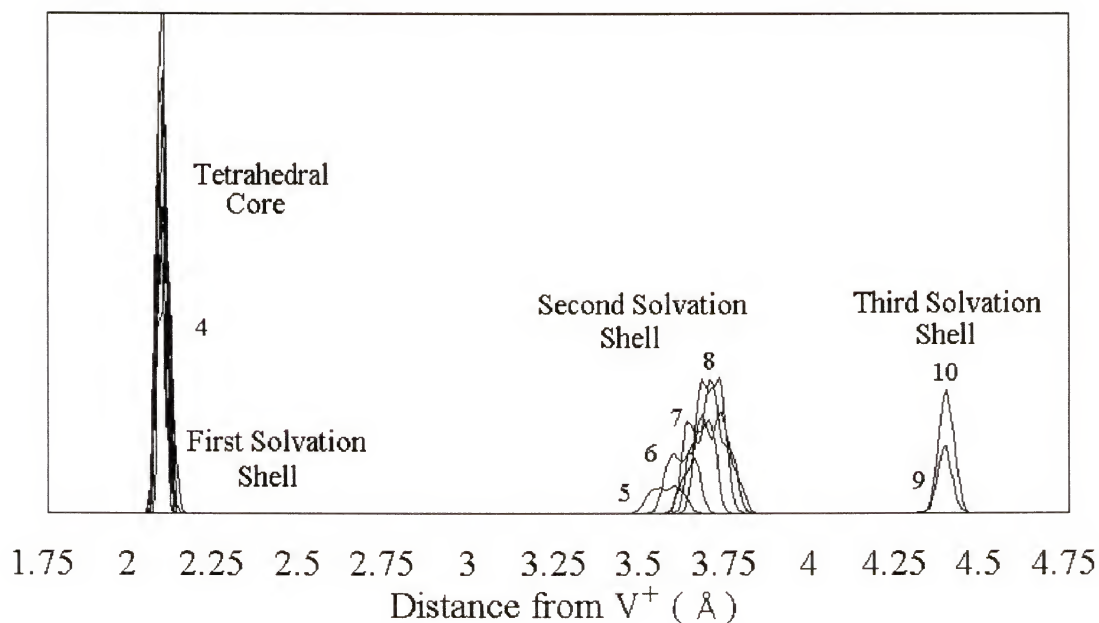


Figure 75. VAr_n^+ (ctet) Radial Distribution.

The figure shows the radial distribution functions from 1.75 to 4.75 $\text{\AA}$ for VAr_n^+ where $n = 4$ to 10. The tetrahedral core is the first solvation shell formed. Four more atoms go into the second solvation shell, which is a tetrahedron capping the first. Six more argons can go into the third solvation shell (only two are shown) which forms an octahedron about the second shell. It is clear that this radial distribution function shows how the argons react to the presence of the others. Of particular interest is the splitting of the second solvation shell with the addition of more argon atoms. Also of note is the increase in average bond length in the second solvation shell as more argons are added, presumably due to the repulsion of nearest neighbors.

where $f(\Gamma_0)$ is the initial distribution function over the phase space.

In particular, the LM^+ atom-pair radial distribution function at time t is

$$g_{LM^+}(r, t) = \frac{V}{N} \left\langle \sum_i \delta[r - r_{LM^+}(t)] \right\rangle. \quad (70)$$

An example of this is shown in **Figure 75**, where the radial distribution function for the argons from the central ion is given for argon 4 to 10.

The time correlation function for properties A and B is also given by the average

$$C_{AB}(t) = \langle A(0)B(t) \rangle = \int d\Gamma_0 A(\Gamma_0) B[\Gamma(t; \Gamma_0)] f(\Gamma_0). \quad (71)$$

Rate coefficients can be obtained following atom-pair distributions versus time, or from the flux autocorrelation function. In what follows, the rates can be determined from concentrations of species defined in terms of statistical averages obtained from molecular dynamics simulations. In these, create a member j , $1 \leq j \leq N_f$ of microcanonical or canonical ensemble by specifying one of N_f initial positions and momenta, and follow the j -th system over time, while calculating the values of its properties. In particular, to obtain the average concentration $[S]$ of species S , we define the species by its conformation and store the conformation of the j -th system at each time interval $[t, t+\Delta t]$. Let $N_s(t)$ be the number of S -conformations found among the N_f systems at that interval; then the concentration of S at time t is defined by

$$[S] = N_s(t)/N_f. \quad (72)$$

More generally, indicating with f the microcanonical or the canonical sampling of initial positions and momenta, averages are given by

$$\langle A(t) \rangle_f = \sum_{j=1}^{N_f} A[\Gamma_j(t; \Gamma_j^0)] / N_f \quad (73)$$

Two types of classical trajectory ensembles come to mind immediately: constant energy and constant temperature. Both microcanonical and canonical dynamics have been used in this study to determine properties of the clusters. The microcanonical method is based upon the velocity Verlet⁶⁵ algorithm,

$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \frac{\mathbf{p}(t)}{m} \Delta t + \frac{\mathbf{F}(t)}{2m} \Delta t^2 \quad (74)$$

$$\mathbf{p}(t+\Delta t) = \mathbf{p}(t) + \frac{1}{2} [\mathbf{F}(t) + \mathbf{F}(t+\Delta t)] \Delta t \quad (75)$$

The canonical molecular dynamics is based upon methods by Nosé⁶⁶ and Hoover⁶⁷. In general, the two methods differ only in the way the system is defined. In the microcanonical system the total energy E is a constant, and the system is only that of the cluster. In the canonical system the total energy E is constant, but the system now contains an additional degree of freedom ζ . This degree of freedom ζ along with a thermal inertia parameter Q are used to force the systems kinetic temperature T_K towards the required temperature T . Thus the additional degree of freedom acts as a heat bath

which can absorb or release energy from the cluster to maintain a relatively constant temperature.

Microcanonical Dynamics

The equations of motion for the microcanonical ensemble are the usual Hamiltonian equations, written here in terms of the forces

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \quad \text{and} \quad \dot{\mathbf{p}}_i = \mathbf{F}_i, \quad \mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij}$$

and are integrated with initial conditions giving a total energy E , which must remain constant over time.

The microcanonical dynamics algorithm proceeds as follows.

1) Pick initial values $\{\mathbf{r}_i\}$ and $\{\mathbf{p}_i\}$ for all atoms i around the oct conformation, such that the system has total momentum $\mathbf{P} = 0$ and total angular momentum $\mathbf{J} = 0$. We impose the former by simply subtracting the total momentum from each of the individual momenta, and the latter by calculating the angular momentum

$$\mathbf{J} = \sum_i (\mathbf{r}_i \times \mathbf{p}_i) \quad (79)$$

and the moment of inertia tensor components (with $\xi, \eta = x, y, z$)

$$I_{\xi\eta} = \sum_{i=0}^n m_i [\delta_{\xi\eta} (\mathbf{r}_i)^2 - (\mathbf{r}_i)_\xi (\mathbf{r}_i)_\eta] \quad (80)$$

solving for the angular velocity vector $\boldsymbol{\omega}$

$$\mathbf{I} \cdot \boldsymbol{\omega} = \mathbf{J} \quad (81)$$

and subtracting its contribution to the individual momenta to obtain the initial values at $t=0$,

$$\mathbf{p}_i^0 = \mathbf{p}_i - m_i(\boldsymbol{\omega} \times \mathbf{r}_i) \quad (82)$$

so that $\mathbf{J}^0 = 0$.

2) Scale the $\{\mathbf{p}_i\}$, multiplying all by a number chosen to make the system have a given total energy $E = K + V$, and set time $t=0$.

3) Step the time variable by Δt .

4) Calculate new $\{\mathbf{r}_i\}$ and $\{\mathbf{p}_i\}$ from

$$\mathbf{p}_i(t+\Delta t) = \mathbf{p}_i + \nabla_i \mathbf{F}_i \Delta t \quad (83)$$

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i + \frac{\mathbf{p}_i}{m_i} \Delta t \quad (84)$$

5) Check for variations in energy. If $E \neq \text{constant}$, reduce time step and go back to previous $\{\mathbf{r}_i\}$ and $\{\mathbf{p}_i\}$ to repeat step (4).

6) If doing constrained minimization, damp momenta by a friction factor (ie. $\mathbf{p}_i' = 0.9\mathbf{p}_i$).

7) Calculate/Store properties.

8) Repeat steps 3-7 until $t=t_{\max}$ or $\{\mathbf{p}_i\} = \mathbf{0}$.

Canonical Dynamics

The equations of motion for the cluster described by a canonical ensemble, at a temperature T , is given by Hamiltonian equations with a time dependent dissipation term,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \quad , \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \zeta \mathbf{p}_i \quad , \quad \dot{\zeta} = \frac{fk_B}{Q}(T_K - T)$$

where ζ is a time-dependent "viscosity", Q is a thermal inertia parameter and the kinetic temperature is given by

$$T_K = \frac{\sum_i \frac{|\mathbf{p}_i|^2}{m_i}}{(3n-6)k_B} \quad (88)$$

where the number of internal degrees of freedom plus the added viscosity variable is

$$f = 3n - 6 + 1 \quad (89)$$

of which one is constrained.

The canonical dynamics algorithm may be carried out as follows.

1) Pick initial $\{\mathbf{r}_i\}$ and $\{\mathbf{p}_i\}$ for all atoms i , such that the system has $\mathbf{J} = 0$ and $\mathbf{P} = 0$ in the manner described above. Pick a T . Choose Q proportional to $k_B(T_{K_{init}} - T)$ and start

with

$$\zeta_{init} = \left(\frac{\sum_i \mathbf{p}_i \cdot \mathbf{F}_i}{\sum_i |\mathbf{p}_i|^2} \right)_{init} \quad (91)$$

- 2) Scale $\{\mathbf{p}_i\}$ to make the system have a given total energy $E = K + V$, and set time $t=0$.
- 3) Step the time variable by Δt .
- 4) Calculate new ζ , $\{\mathbf{r}_i\}$ and $\{\mathbf{p}_i\}$ from

$$\mathbf{p}_i(t+\Delta t) = \mathbf{p}_i + \mathbf{F}_i \Delta t - \zeta \mathbf{p}_i \Delta t \quad (92)$$

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i + \frac{\mathbf{p}_i}{m_i} \Delta t \quad (93)$$

$$\zeta(t+\Delta t) = \zeta + \frac{fk_B}{Q} (T_K - T) \Delta t \quad (94)$$

- 5) Verify that $T_K \rightarrow T$, by requiring that the average and standard deviation of $(T_K - T)$ over a set of earlier times are small. If not repeat 3-5 until the thermalization time t_{therm} .
- 6) Calculate/Store properties.
- 7) Repeat steps 3-5 until the cluster has reached its final state at $t = t_{\text{max}}$.

Application to the Isomerization of VAr_6^+

The unique short range ordering and various long range interactions among atoms in solution chemistry present formidable problems. It is hoped that by modeling systems,

which are chosen to simplify the atomic interactions, we can achieve a detailed description of solvation. Solvent-solute behavior in the condensed phase has been modeled by various research groups.^{33,8,13,1,68} The interactions of an ion with solvent molecules is of considerable interest, since most "ionic" reactions take place in solution. The simplest ion-solvent interaction one might think of is one where complicated ion-dipole and or covalent interactions have been removed. For this reason a transition metal ion solvated in a rare gas makes a convenient pedagogical model. In this example application VAr_6^+ is chosen because previous calculations⁶⁹ indicated that there were two nearly isoenergetic minima, a capped tetrahedron (**ctet**) and an octahedron (**oct**), shown in **Figure 76** upper left and lower right respectively. The octahedral isomer was predicted to be the global potential energy minimum. This example examines how each of these conformations change by determining the barrier to isomerization and the rate at which isomerization occurs, using two methods. In the calculations, interactions are modeled by using simple Lennard-Jones 12-6 potentials for the weak Ar-Ar interaction and a Lennard-Jones 8-4 potential fit to spectroscopic data for the V^+ -Ar interaction¹³.

Various groups have made calculations of rates of reaction. Berry et al.⁷⁰ have investigated "freezing and melting" in Ar_n clusters. Rice et al.⁷¹ have developed extended methods for unimolecular isomerization. Jortner et al.⁷² have investigated time-resolved dynamics of cluster isomerization.

We have chosen to model simple cation clusters such as $\text{M}^+(\text{L})_n$, (M = metal and L = a rare gas or small molecule). In this example the Ar 'ligands' are used to effectively eliminate long range dipole-dipole interactions and leave primarily charge-induced dipole

and van der Waals interactions. Simple clusters like these have been investigated with a variety of experimental and theoretical techniques. Only recently have spectroscopic studies of diatomic transition metal rare-gas cations given the details of the potential energy surface (PES) necessary for accurate computer modeling. Monte Carlo (MC) type algorithms have proven effective in modeling simple homogenous solutions.⁷³ Simulated annealing (SA), a variation of MC, has been used by us to model equilibrium properties of more complicated systems such as $M^+(L)_n$ as shown in the previous chapter.

In this and previous studies experimentally determined potentials have been taken for VAr^+ and Ar-Ar as the two pair potentials to model a 'solvated' transition metal cation in the gas phase. Previously, in a preliminary work, a lower bound to the isomerization energy barrier was determined, and a rough estimate of the activated complex conformation of VAr_6^+ with constrained SA and molecular dynamics (MD).⁷⁴ This study is now concerned with determining the isomerization barrier and finding the thermal rates of isomerization for the complex. The two lowest potential energy minima correspond to octahedral $(V^+)Ar_6$ and capped tetrahedral $(V^+)Ar_4Ar_2$ isomers, thus the interest in the isomerization reaction:



The octahedral complex is bound by about 0.015eV more than the capped tetrahedral, demonstrated in **Figure 74**. At a given temperature both isomers are present because entropy favors the capped tetrahedral complex. Hence, even at relatively low

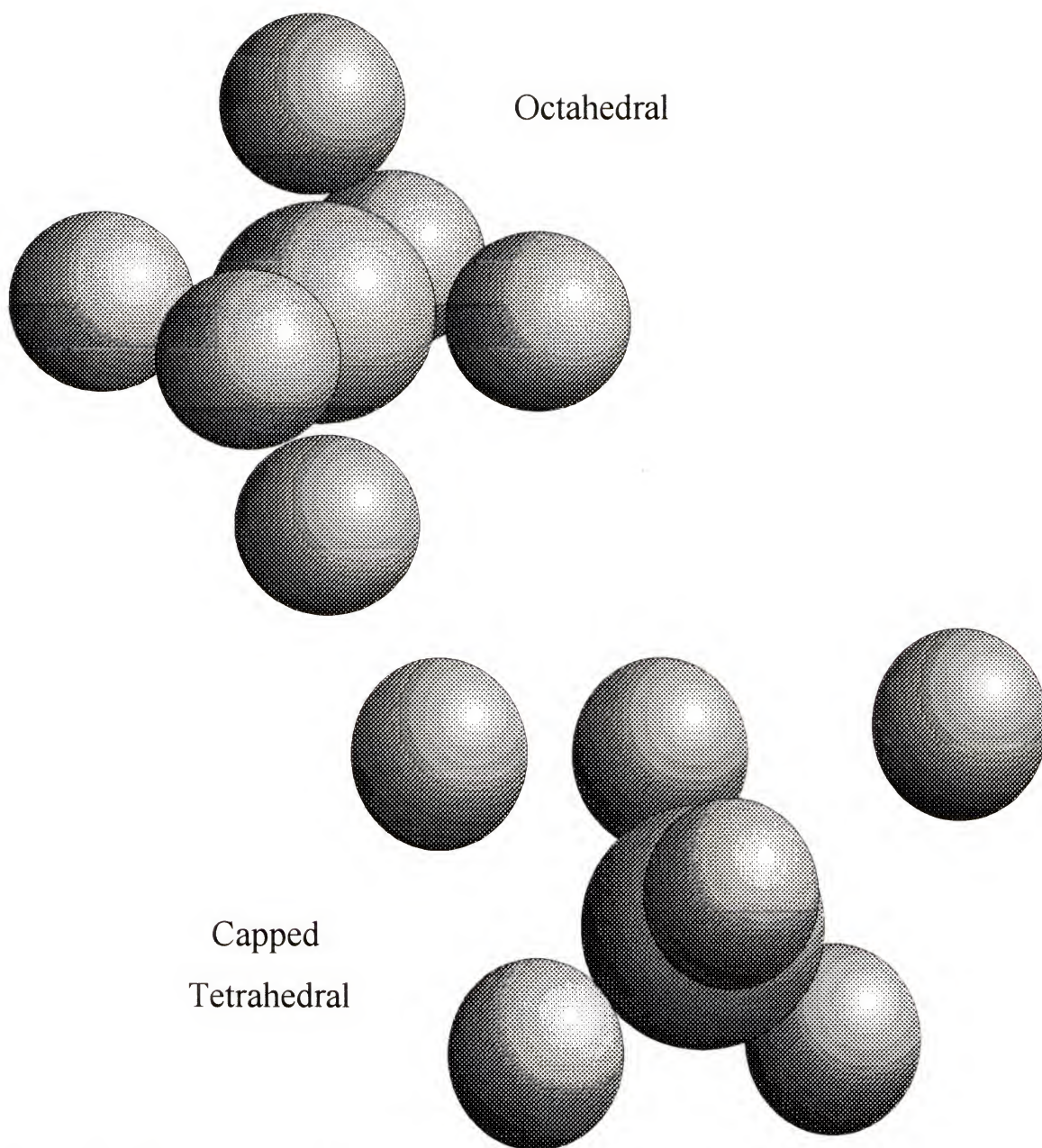


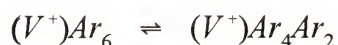
Figure 76. The octahedral VAr_6^+ (**oct**) and the capped tetrahedral $\text{VAr}_4\text{Ar}_2^+$ (**ctet**) complexes.

The upper left figure shows the most stable isomer of VAr_6^+ , the octahedral configuration. The lower right is the next lowest potential energy structure, the capped tetrahedral configuration. The abbreviations **oct** and **ctet** are used widely in the text. The two geometries have been minimized using damped classical trajectories and simulated annealing.

temperatures, the capped tetrahedral configuration dominates the phase space. Compared below are microcanonical and canonical isomerization rates from fixed energy and fixed temperature MD.

Isomerization Barriers

Two methods have been used to map out the PES around the transition state of the



isomerization in order to estimate the barrier between the octahedral and bicapped tetrahedral isomers. The two methods used to do this are constrained simulated annealing and constrained molecular dynamics. Once a picture of what the barrier looks like has been determined, rates of reaction/isomerization can be extracted from molecular dynamics calculations by monitoring the atoms in various solvation shells versus time. The approximate solvation shells for V^+ have been described previously⁷⁵. The VAr_6^+ with the potentials listed above has inner shell closings at 4 (a tetrahedron) or 6 (an octahedron). For VAr_6^+ we monitor the number of clusters which have $n=1-6$ Ar atoms in the first (inner) shell, N_1 , closest to the V^+ ion versus time. The inner shell is defined by a sphere of 3 Å in radius centered on the V^+ ion and will be justified below. As the isomerization **oct** → **ctet** proceeds, N_1 decreases from 6 to 4.

Nearest Neighbor Counting

Some effort has been devoted to determining the optimum size for the nearest neighbor criterion. Classical trajectory calculations were done to determine the radial distribution functions and thus dynamic structure of the VAr_6^+ cluster. These distribution functions have been obtained for both the **oct** and **ctet** configurations (see **Figure 77** and **Figure 78**) at energies too low to cause isomerization. These plots of probability versus distance give physical meaning to the terms “inner shell” and “solvation shells”. For both the **oct** and **ctet** the inner shell, N_1 , is within $3\text{\AA}$ of the V^+ . We have chosen to call all atoms within this sphere the nearest neighbors for the trajectories. In the distribution functions for the two isomers it is clear that this inner shell is within the $3\text{\AA}$ we have chosen, and that the capping atoms of the capped tetrahedral complex lie considerably outside this distance. Additionally, changing this distance by $\pm 0.2\text{\AA}$ has only a slight effect on the results we obtain. If we look at the minimized potential energy plot versus one fixed $r(V^+-Ar)$ distance, in **Figure 74**, it is clear that this choice is close to the pseudocrossing at $3.08\text{\AA}$.

Isomerization Rates

Isomerization rates can be extracted directly from the concentrations of the products and reactants versus time with various constant energies and temperatures. The isomerization can be viewed as simply reactants going to products with no intermediates. For this case, complexes with nearest neighbor numbers of more than 4 argons are considered unreacted (ie. still in the minimum of the octahedral). So the classical kinetics equation is:

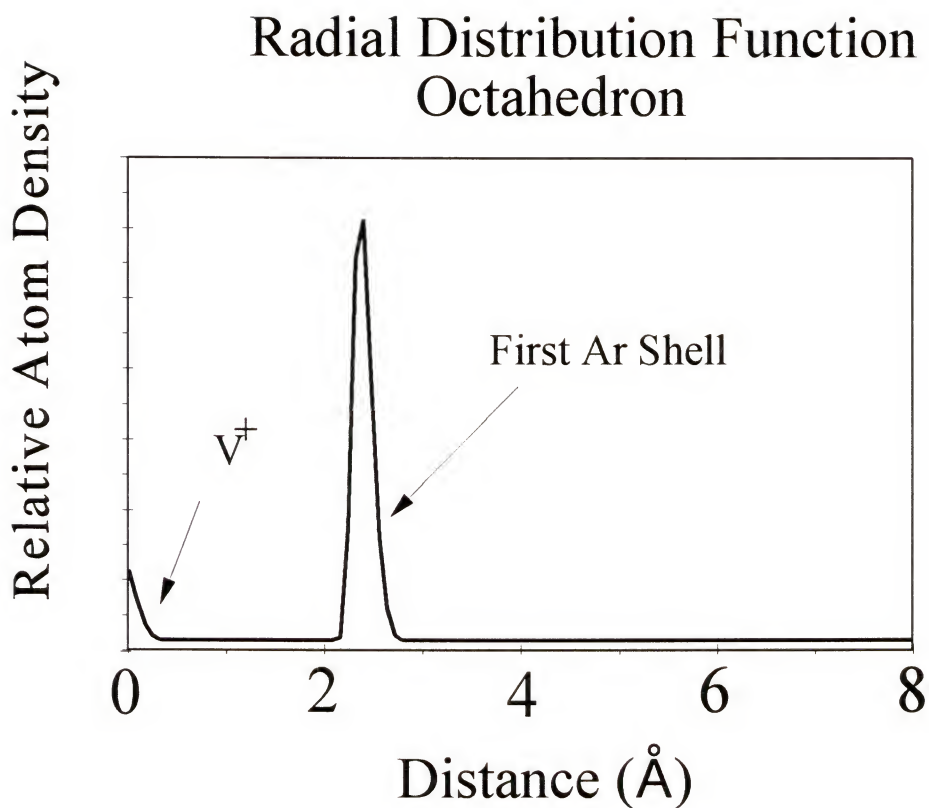


Figure 77. The VAr_6^{+} Octahedral Radial Distribution Function.

The figure shows a plot of the radial distribution function for the octahedral VAr_6^{+} complex. The function is averaged during a molecular dynamics trajectory calculation with a small excitation.

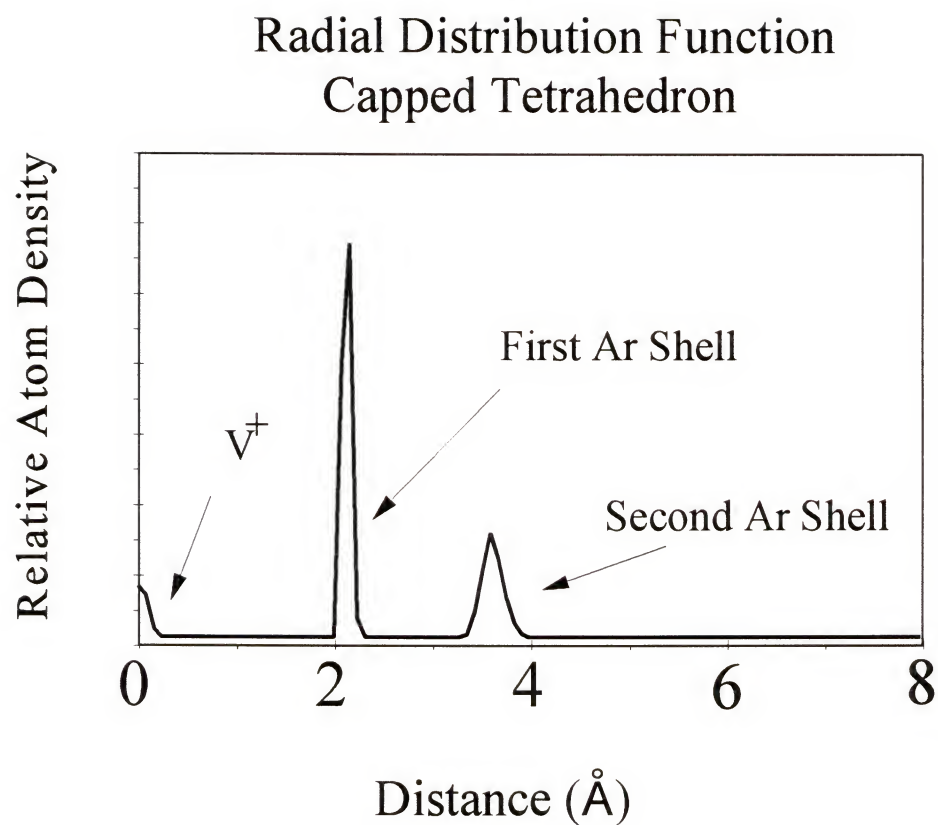
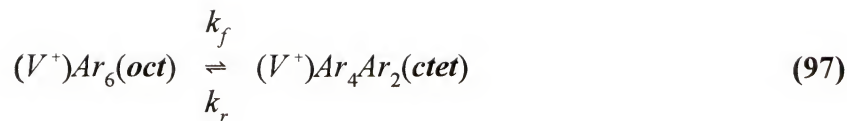
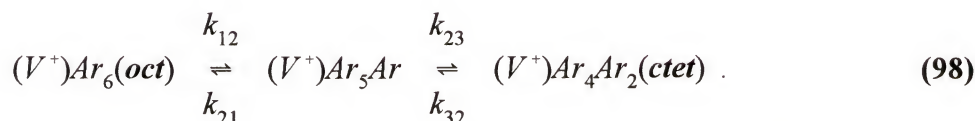


Figure 78. Capped Tetrahedral VAr_6^+ Radial Distribution.

The figure shows the capped tetrahedral VAr_6^+ isomer. Distribution functions can reveal various details about the cluster. In this and the previous figure it can be seen that the first solvation shell falls within $3\text{\AA}$. Determining where the various solvation shells occur in the clusters help in the modeling of isomerization.



Careful counting of nearest neighbors, however, gives evidence of an intermediate with 5 argons which can be monitored in the short time region. In this case, one Ar has moved away from octahedral minimum (with the other soon to follow) and the kinetics equation is:



Isomerization data for both circumstances, with and without intermediates, has been analyzed.

Several methods of extracting the isomerization rate can be envisioned. One method would be to start from the rate constant as it relates to the flux-flux time correlation function, which leads to a simple expression in terms of the transition state properties. Other methods can be based upon the various properties of the clusters that have been extracted during the MD calculations described above. In the next two sections, it will be shown how rates can be extracted from the microcanonical and canonical ensembles.

Rate Coefficients with No Intermediates

Monitoring only the reactants (but no intermediates) in a microcanonical MD simulation, we can interpolate smoothly by least squares fit through a time series, to fit results with the function

$$\ln[Var_6^+(t)] = k_\mu(E)(t-t_0) \quad (99)$$

where k_μ is a microcanonical rate coefficient; this is indicative of first order kinetics.

Repeating the simulation for various values of E we can parametrize the rate coefficient as

$$k_\mu(E) = A_\mu \exp(-E_\mu/E), \quad E \geq V_{psc} \quad (100)$$

$$k_\mu(E) = 0, \quad E < V_{psc} \quad (101)$$

If the intermediate behavior is modeled there are four rate constants which depend upon E : $k_{12}(E)$, $k_{21}(E)$, $k_{23}(E)$ and $k_{32}(E)$. The kinetic equations used to model the data are outlined below.

The MD simulations at fixed T give similar results to those at constant E , and the same treatment can be applied when ignoring intermediate concentration.

$$\ln[Var_6^+(t)] = k_c(T)(t-t_0) \quad (102)$$

where k_c is a canonical rate coefficient; which is also indicative of first order kinetics.

Repeating the simulation for various values of T , the rate coefficient with the Arrhenius expression can be parameterized

$$k_c(T) = A_c \exp(-U_c/k_B T) \quad (103)$$

where U_c is the internal energy for activation.

If the intermediate behavior is modeled, as before, four rate coefficients are obtained which depend upon T : $k_{12}(T)$, $k_{21}(T)$, $k_{23}(T)$ and $k_{32}(T)$.

Kinetic Isomerization Equations with an Intermediate

If we consider the general isomerization reaction



with initial conditions

$$t=0, [A_1]=[A_1]_0, [A_2]_0=[A_3]_0=0 \quad (105)$$

and

$$[A_1]_0=[A_1]+[A_2]+[A_3] \quad (106)$$

we obtain differential equations of the following form^{76,77}

Concentration Contour Plot

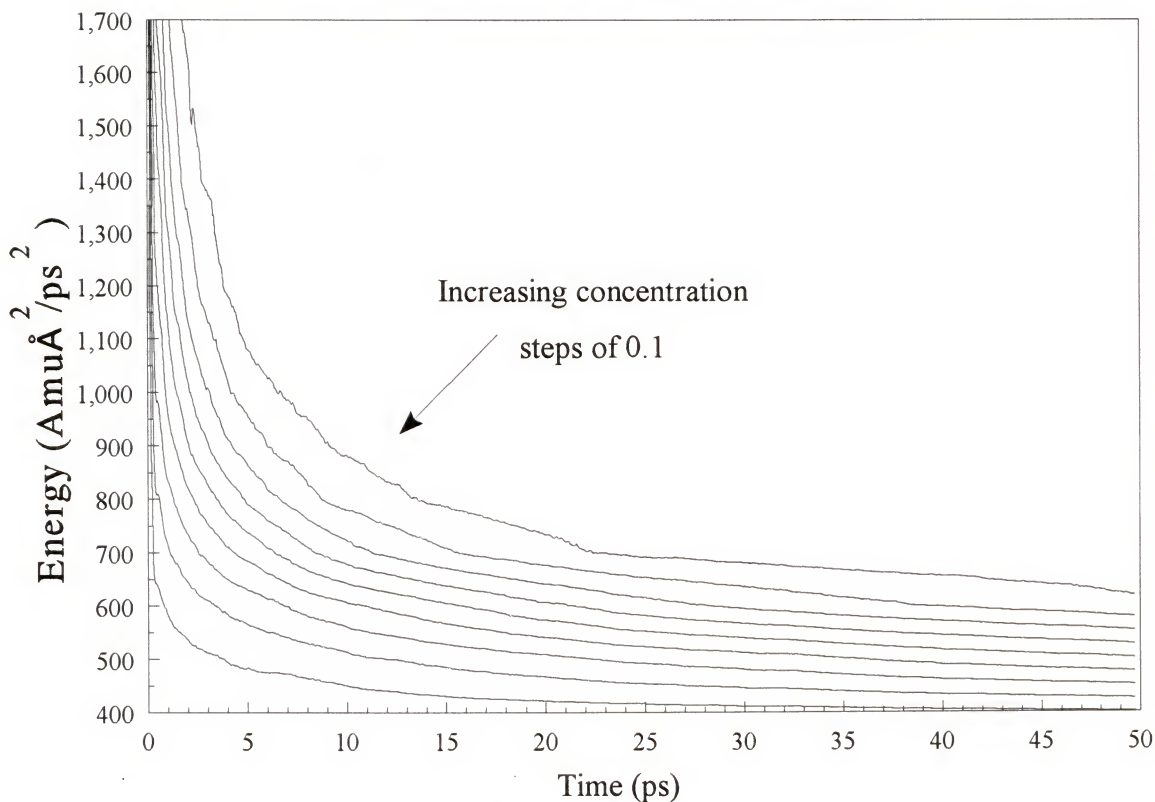


Figure 79. VAr_6^+ Octahedral Isomerization Contour Plot.

The figure shows the concentration of VAr_6^+ **oct** contour plot. The plot is constructed from data obtained in the microcanonical trajectories from 400 to 1700 $\text{Amu}\text{\AA}^2/\text{ps}^2$ versus time from 0 to 50 ps. The concentration contours are in steps of 0.1 from 0 to 1. It is clear that the concentration of VAr_6^+ **oct** decreases rapidly as the excitation energy increases.

$$\frac{d[A_1]}{dt} = k_{21}[A_2] - k_1[A_1] \quad (107)$$

$$\frac{d[A_2]}{dt} = k_{12}[A_1] - k_{21}[A_2] - k_{23}[A_2] + k_{32}[A_3] \quad (108)$$

$$\frac{d[A_3]}{dt} = k_{23}[A_2] - k_{32}[A_3] \quad (109)$$

The solution of these gives, with $s = 1, 2, 3$,

$$[A_s] = A_{s1} + A_{s2} \exp[-\lambda_2 t] + A_{s3} \exp[-\lambda_3 t] + [A_1]_0 \quad (110)$$

and

$$A_{11} = \frac{k_{21}k_{32}}{\lambda_2\lambda_3}, \quad A_{21} = \frac{k_{12}k_{32}}{\lambda_2\lambda_3}, \quad A_{31} = \frac{k_{12}k_{23}}{\lambda_2\lambda_3} \quad (111)$$

$$A_{12} = \frac{k_{12}(\lambda_2 - k_{23} - k_{32})}{\lambda_2(\lambda_2 - \lambda_3)}, \quad A_{22} = \frac{k_{12}(k_{32} - \lambda_2)}{\lambda_2(\lambda_2 - \lambda_3)}, \quad A_{32} = \frac{k_{12}k_{23}}{\lambda_2(\lambda_2 - \lambda_3)}, \quad (112)$$

$$A_{13} = \frac{k_{12}(k_{23} - k_{32} - \lambda_3)}{\lambda_3(\lambda_2 - \lambda_3)}, \quad A_{23} = \frac{k_{12}(\lambda_3 - k_{32})}{\lambda_3(\lambda_2 - \lambda_3)}, \quad A_{33} = -\frac{k_{12}k_{23}}{\lambda_3(\lambda_2 - \lambda_3)}, \quad (113)$$

where

$$\lambda_2 = \frac{(p+q)}{2}, \quad \lambda_3 = \frac{(p-q)}{2}, \quad p = k_{12} + k_{21} + k_{23} + k_{32}, \quad q = [p^2 + (k_{12}k_{23} + k_{21}k_{32} + k_{12}k_{32})]^{1/2} \quad (114)$$

Isomerization Results

The data from the microcanonical and canonical dynamics have been fit with the assumption of no intermediates and considering isomerization intermediates. The canonical trajectories have been carried out for temperatures from 40 to 200K and the microcanonical trajectories have been carried out for internal energies of 400 to 1700 AmuÅ²/ps². A contour plot of the **oct** concentration from the microcanonical trajectories is shown in **Figure 79**. The contours are increasing concentration in the direction of the arrow and indicate a rapid decay of the **oct** complex at high energy and a slower decay at low energy. A contour plot for canonical trajectories is similar and is not shown here. The simple first order kinetics which arise from treating only the decay of reactant, VAr₆⁺ **oct**, in the microcanonical trajectory average at 1000 AmuÅ²/ps² has been plotted in **Figure 80**. Both the microcanonical and canonical trajectories show evidence for an intermediate which is neither coordination number 4 or 6. This is more pronounced in the canonical trajectories. A fit of the decay of the **oct** for a 100 K canonical trajectory reveals that a minimum of a two step decay is taking place, shown in **Figure 81**. Closer examination of each species and not just the reactant in **Figure 80** or **Figure 81**, indicates that there are oscillations in the all of the species in the short time region. Fitting to the short time behavior is very difficult and may not be possible because the kinetics equations used to fit the data do not take into consideration rearrangement times. For this reason the data has been fit from time 0.5ps into the trajectories. The 100 K canonical average data for each species has been simultaneously fit in **Figure 82**, which shows these oscillations. The fit is clearly poor in the short time region. This is probably due to

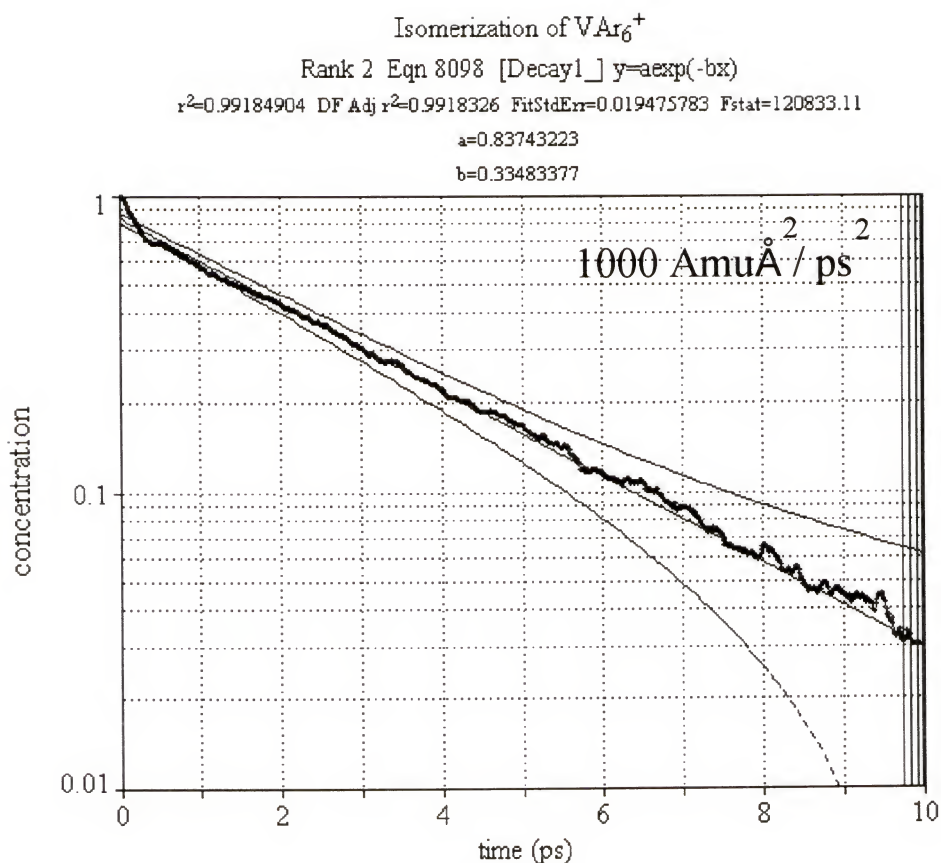


Figure 80. Fit to Microcanonical Trajectory Average.

The figure shows the concentration of VAr_6^+ oct from an average of 1000 microcanonical trajectories at $1000 \text{ Amu}\text{\AA}^2/\text{ps}^2$ versus time from 0 to 10 ps. The concentration decreases rapidly at this energy, and the fit with error bars indicates only a simple decay.

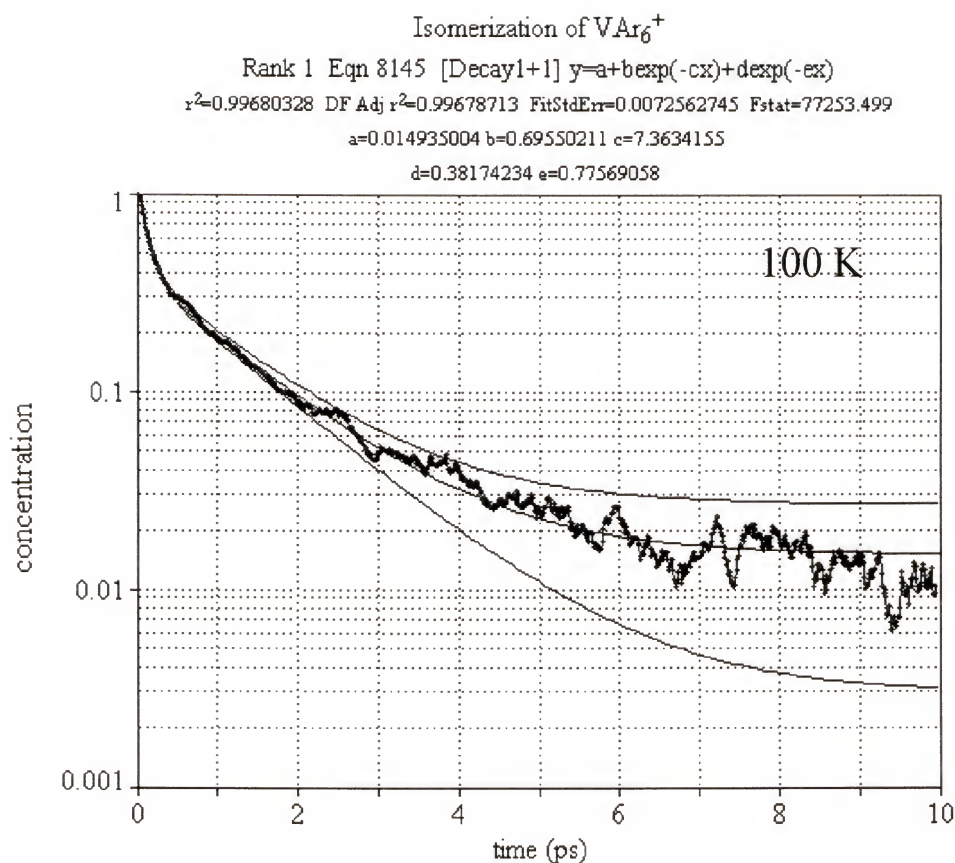


Figure 81. Canonical Isomerization of VAr_6^+ .

The figure shows the concentration of VAr_6^+ oct from an average of 1000 canonical trajectories at 100K versus time from 0 to 10 ps. The concentration decreases rapidly at this temperature, and the fit with error bars indicates at least a two step decay. A fit to the exact equations including the intermediate are shown in another figure.

intramolecular rearrangement occurring in the short time region. The simple kinetic theory used here does not model this behavior but it is certainly taking place. The energy and temperature dependent rates for fits to the long time behavior have been plotted in **Figure 83** and **Figure 84**, respectively.

MD provides a tractable approach to solving large solvation systems where some of the interactions have been removed. This work represents an alternative to the calculation of thermal rates from flux-flux autocorrelation functions. The derived thermal rates could be used to check the validity of transition state approximations. Additional information can be obtained during the simulation, such as power spectra, radial distributions, etc. Constrained SA and MD help place a lower bound on the isomerization barrier.

The MD algorithm calculates the momenta and positions of all the atoms at each time step. Taking their Fourier transforms, we can calculate a power spectrum of their momenta or positions and obtain from them all of the vibrational frequencies, insofar as all the degrees of freedom are expected to strongly couple in the clusters. Following this procedure for the two isomers of VAr_6^+ , a plot of each of the modes (not only the normal modes) is obtained, as in **Figure 85**.

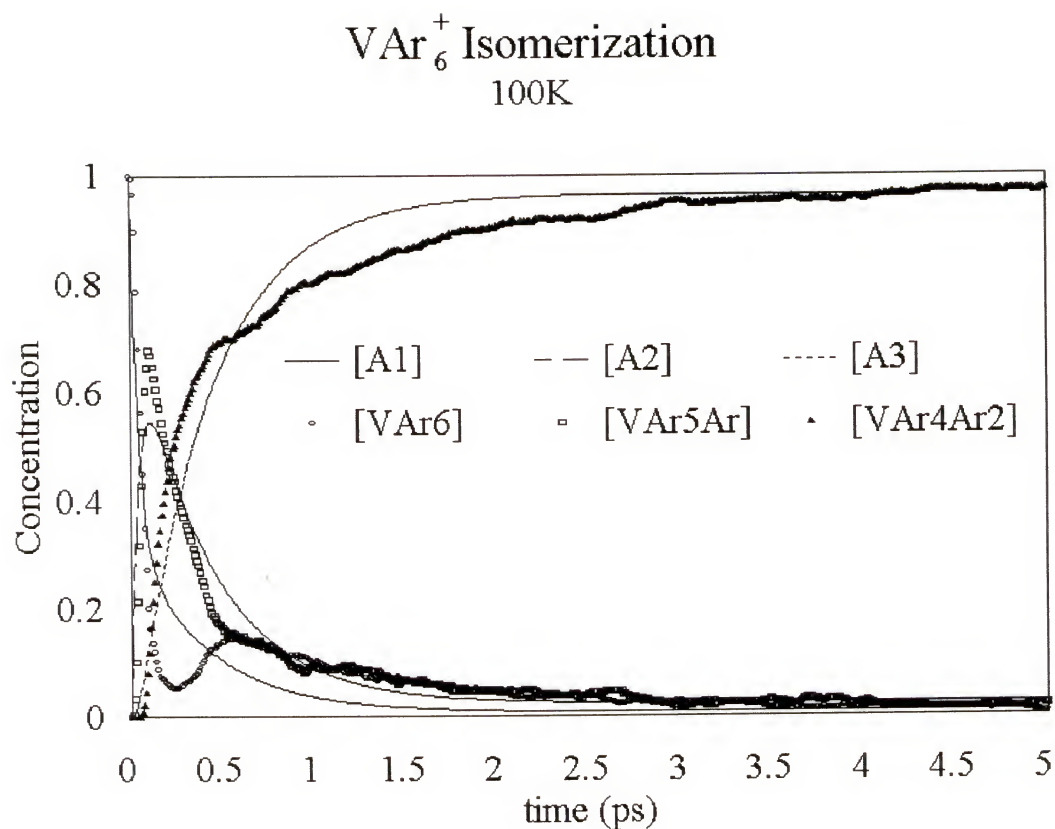


Figure 82. VAr_6^+ , VAr_5Ar^+ and $\text{VAr}_4\text{Ar}_2^+$ Concentrations with Fit.

The figure shows the concentration of VAr_6^+ **oct**, VAr_5Ar^+ and $\text{VAr}_4\text{Ar}_2^+$ **ctet** (symbols) with the simultaneous fit for each (lines). The fit in the short time region is poor, but the long time behavior is modeled well. The poor fit in short time is most likely due to intermolecular rearrangement which the kinetic theory, used to model the behavior, does not include.

Microcanonical Rates vs Energy

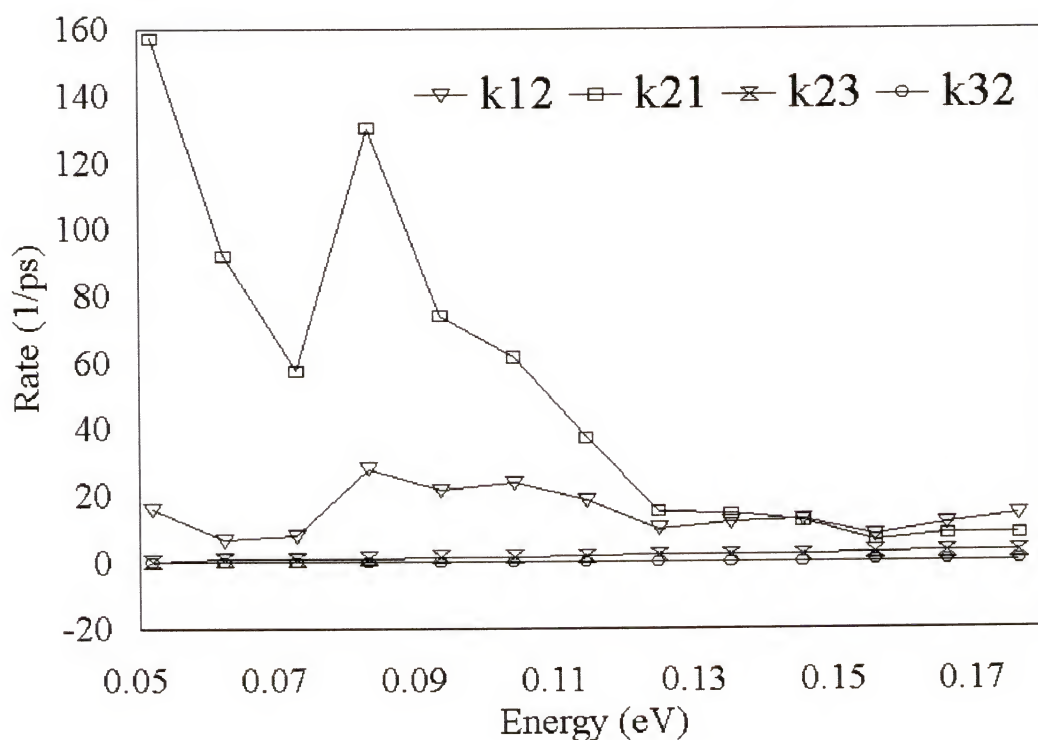


Figure 83. Rate Constants from Fits to the Microcanonical Trajectories.

The figure shows the rate constants k_{12} , k_{21} , k_{23} and k_{32} from the simultaneous fit for each averaged microcanonical trajectory from 400 to 1800 AmuÅ²/ps² (converted here to eV). The fits were done to model the long time behavior; the short time fit is poor.

Canonical Rates vs Temperature

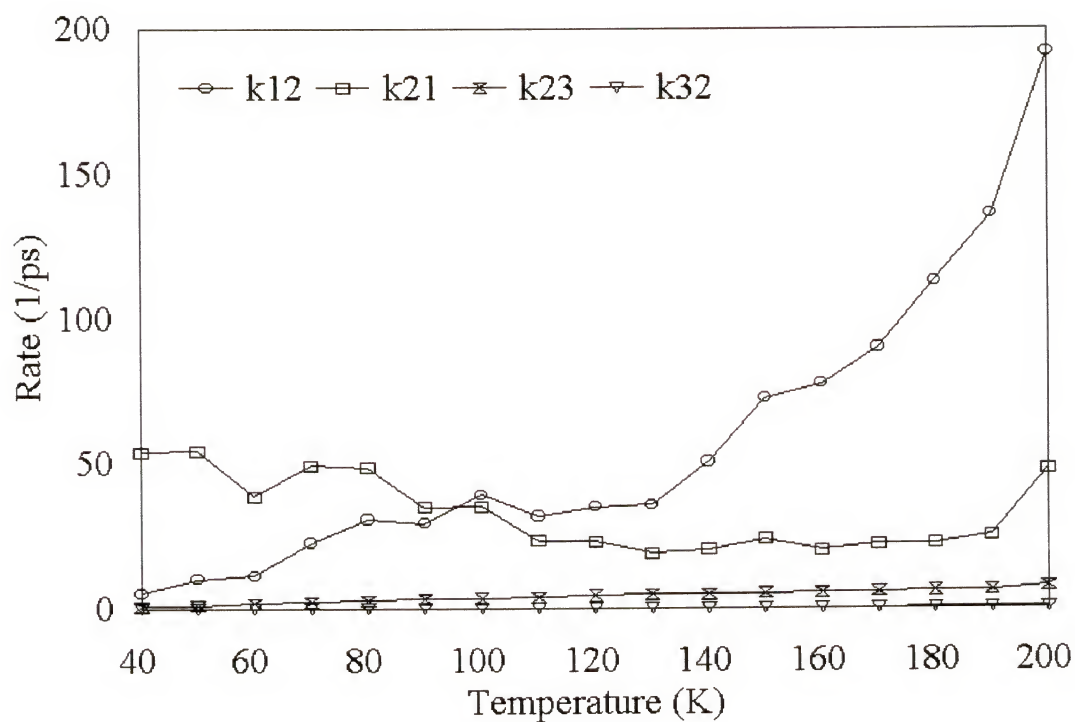


Figure 84. Rate Constants from Fits to Canonical Trajectories.

The figure shows the rate constants k_{12} , k_{21} , k_{23} and k_{32} from the simultaneous fit for each averaged microcanonical trajectory from 40 to 200 K. The fits were also done to model the long time behavior.

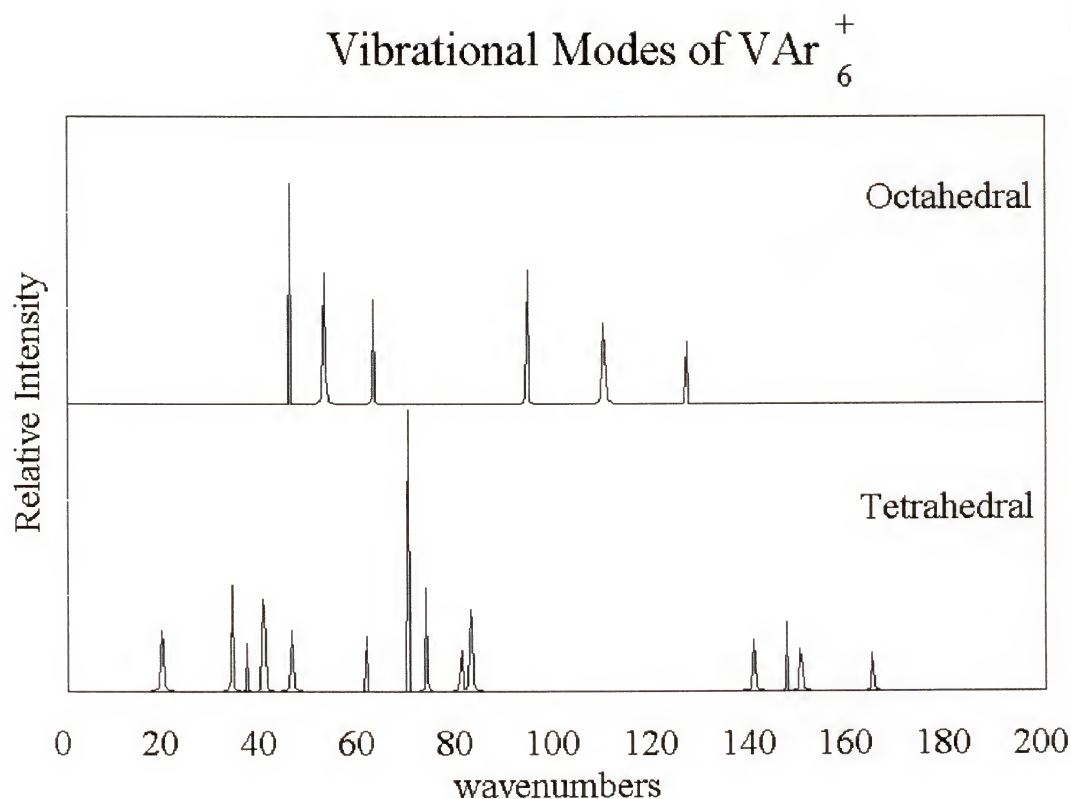


Figure 85. VAr_6^+ oct and $\text{VAr}_4\text{Ar}_2^+$ **ctet** Modes.

The figure shows the power spectrum of the momenta monitored during the trajectories for the **oct** and **ctet** configurations. The trajectories were run under low excitation as is done for typical normal mode analysis. These spectra give all of the $3N-6 = 3 \cdot 7 - 6 = 13$ modes of each configuration. The **oct** shows only 6 modes and it is clear that some of the modes are degenerate. The **ctet** shows all 13 modes, one of which is slightly split. All of the modes are very low energy (less than 200cm^{-1}) as might be expected for floppy molecules such as these.

CHAPTER 8 CONCLUSIONS

This dissertation was designed to tell how small cluster of transition metal cations cluster with small molecule(s) or rare gas atom(s). Two attempts at exploring these cluster ions has been presented. The first showed the experimental methods which allowed these clusters to be made and analyzed spectroscopically. The second investigated theoretical methods of modeling these clusters with classical potentials. The two methods combined to give a beginning point for new experiments and calculations which will inevitably become cheaper.

The experimental chapters detail how thermally unstable clusters have been formed in a kinetically limited source and analyzed in the gas phase. The photodissociation spectra in these chapters give graphic illustration of the quantal ro-vibronic levels in these systems. Table XXII and Table XXIII, which detail the results of the diatomic systems and the polyatomic systems respectively, help summarize the results.

The first system presented in this dissertation, CoAr^+ , had the most interesting spectra, since they were rotationally resolved for nearly the entire A' state. The extra information provided by the rotational analysis is invaluable since it allows the determination one of the more important properties in chemistry, the ground and excited state bond lengths.

Table XXII. Diatomic Molecular Spectroscopy Constants for New Systems.

Ion	State Label	Atomic State	Molecular State	T_{e0} cm^{-1}	D cm^{-1}	D_e cm^{-1}	r_e $\text{\AA}$	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}
CoAr ⁺	X	Co ⁺ d ⁸ ³ F ₃ +Ar ¹ S	³ Δ_3			4111±5	2.385 ⁱ		
	a	Co ⁺ d ⁸ ¹ D ₂ +Ar ¹ S	¹ Δ_2	12493			2.458 ⁱ	120	
	A'	Co ⁺ d ⁷ s ³ F ₄ +Ar ¹ S	³ Φ_4	12353	13920	1567	2.784	104	2.07
	B'	Co ⁺ d ⁸ ³ F ₃ +Ar ¹ S		12808			<2.74	160	2.14
	b	Co ⁺ d ⁸ ¹ D+Ar ¹ S		13081		2677		165	3.20
	B	Co ⁺ d ⁷ s ³ F ₂ +Ar ¹ S	³ Φ_2	13380	15433	2053		121	2.21
	C	Co ⁺ d ⁸ ³ P ₂ +Ar ¹ S	³ Π_2	14458	17370	2912		176	3.28
ZrAr ⁺	X	Zr ⁺ d ² s ⁴ F _{3/2} +Ar ¹ S	⁴ $\Phi_{3/2}$			2690±20	2.710 ⁱ		
	a		? _{3/2}	14829			<3.47	65.7	0.48
	b		? _{1/2}	14911			<3.05	129	2.17
	d'		? _{5/2}	15489			<3.32	63.1	0.21
	c	Zr ⁺ d ³ ² G _{7/2} +Ar ¹ S	? _{5/2}	15550	16765	1215	3.037	72.6	0.81
	d	Zr ⁺ d ³ ² D _{7/2} +Ar ¹ S	? _{5/2}	15686	16869	1183	<4.20	60.4	0.42
NiAr ⁺	X	Ni ⁺ d ⁹ ² D _{5/2} +Ar ¹ S		-113±25		4685±25		225±50	
	a	Ni ⁺ d ⁸ s ⁴ F _{7/2} +Ar ¹ S		11977	13903	1926		118	2.23
	b	Ni ⁺ d ⁸ s ⁴ F _{7/2} +Ar ¹ S		12031	13903	1872		115	2.18
	c	Ni ⁺ d ⁸ s ⁴ F _{5/2} +Ar ¹ S		12902	14688	1786		113	2.27
CoXe ⁺	X	Co ⁺ d ⁸ ³ F ₃ +Xe ¹ S	³ Δ_3				2.880 ⁱ		
	a	Co ⁺ d ⁸ ¹ D ₂ +Xe ¹ S	¹ Δ_2				2.883 ⁱ		
	A			12968				123	0.80
	B			13684				124	0.74
	C			13839				186	3.90
	D			14078				128	0.79
	E			14951				160	1.06
Ni ₂ ⁺	X					18900±100 ⁱⁱ	2.25±0.07 ⁱ		

ⁱ r_0 's reported for these states.ⁱⁱ D₀ reported for these states.

The NiAr⁺ system was the first Ni⁺ system which had resolvable vibrational spectra. The system also had first known spin forbidden transitions observed in our group. The very weak transitions observed here demonstrate the how the hemispherical sector improved the detection limits of the present apparatus. This system provides direct information about the states observed. The red cutoffs observed correspond to the

dissociation limits from the $\text{Ni}^+ \text{}^4\text{F}_{9/2}$, $\text{}^4\text{F}_{7/2}$ and $\text{}^4\text{F}_{5/2} + \text{Ar } ^1\text{S}$. The isotopomers allow for the absolute vibrational assignments and determination of excited state parameters.

ZrAr^+ has provided some insight into how heavier (ie second row) transition metal systems differ from previously investigated systems like VAr^+ , CoAr^+ and NiAr^+ . The intensity of the spin forbidden transitions seen here belie a greater “allowedness” than those seen in the NiAr^+ . The two dissociation limits observed in this system were a great aid in determining the ground state bond energy, and the two excited state bond energies. The rotational resolution was an unexpected bonus obtained while trying to get good isotopic shifts. This rotational data is evidence that these states are longer lived than those of many of the systems previously investigated in this group. Though bond lengths of every state have not been determined, an upper limit has been set by the values of the rotational constants obtained by the lowest observed ro-vibronic bands of each state.

Though there are several details revealed about the CoXe^+ system, it clear that this system requires further investigation. Perhaps the most interesting feature of this cluster is the similarity of the a state to that found in the CoAr^+ cluster and very recently in the CoKr^+ cluster. This state, while not fully rotationally resolved in the CoXe^+ cluster, has been fit well, to give both an ground and upper state r_0 . The bond lengths of this cluster are slightly larger than the CoAr^+ . The newly observed CoKr^+ a state is fully resolved, which helped confirm the identity of the state, and has a bond length which lies between the two as might be expected. Identification of the other states in this system appears to be relatively straight forward with only a little more work. Rotational analysis for large v' of CoXe^+ would most likely provide new and useful information.

The states observed in $\text{Co}\cdot\text{CO}_2^+$ are certainly similar to those observed in CoAr^+ .

The spin forbidden $\tilde{a}-\tilde{X}$

$\text{Co}\cdot\text{N}_2^+$ provides an interesting case of a T-shaped molecule, which becomes linear as v' becomes large. Solvation of ions in liquid nitrogen should perhaps behave in a similar manner. The potential provided in Chapter 4, should allow for simple and generally accurate modeling. The modeling which was presented in this dissertation has been carried out concurrently with the experimental investigations. The insights gained from this system allow the simplest step forward in this modeling since there is no permanent dipole but there are quadrupole and nonsymmetrical polarizabilities.

Direct evidence of the $\text{Ni}\cdot\text{CO}_2^+$ bond energy has been observed but the spectrum remains unanalysed. There is clearly a resonant dissociation spectrum which can and should be analyzed. The isotope shift and dissociation threshold here provide most of the information reported in this dissertation.

The $\text{Ni}\cdot\text{H}_2\text{O}^+$ and $\text{Co}\cdot\text{H}_2\text{O}^+$ systems provided less direct information. The full rotational analysis of these systems will provide the most important information to be gained from these systems. Since the $\text{M}\cdot\text{HOD}^+$ spectra appear relatively unchanged from the $\text{M}\cdot\text{H}_2\text{O}^+$ and $\text{M}\cdot\text{D}_2\text{O}^+$ spectra, for both systems, it seems clear that the geometry is C_{2v} . The vibrational analysis is similar for the systems as well, with vibrational progressions of $>300\text{ cm}^{-1}$. The rotational data need only be fit for the various vibrational levels to obtain values for centrifugal distortion of the $\text{Ni}\cdot\text{H}_2\text{O}^+$. Once this has been accomplished a potential energy surface could be constructed, allowing for the modeling water solvation.

Table XXIII. Polyatomic Molecular Spectroscopy Constants for New Systems.

Ion	State Label	T_{e0} cm^{-1}	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}	D_e cm^{-1}	Geometry
$\text{Ni}\cdot\text{H}_2\text{O}^+$	X					C_{2v}
	A	16715	350	2.78		
	B	18150	348	2.45		
$\text{Co}\cdot\text{H}_2\text{O}^+$	X					C_{2v}
	A	13687	305	1.38		
	B	13806	319	2.11		
	C	15718	336	4.20		
	D	15882	329	2.66		
$\text{Ni}\cdot\text{CO}_2^+$	X				8700 ± 100	
$\text{Co}\cdot\text{N}_2^+$	X					T-shaped C_{2v}
	a	13297				
	B	15500	140	-1.24	3900	
$\text{Co}\cdot\text{CO}_2^+$	X					Linear $\text{C}_{\infty v}$
	a	12301				
	A'	12375	190	-2.45	4400	
	B'	13660	181	-2.83		
	B	14883	258	10.26		
	C	15051	213	3.03		
	D	15081	193	-3.79		

The conclusions arrived at for Ni_2^+ have taken several groups and years to complete. The bond strength given in this dissertation is felt to be the best determination to date. In addition the ground state bond length has been determined. The quality of these two parameters renew the call for good *ab initio* calculations.

Simulated annealing gave a way to model larger systems at zero Kelvin. While these gave no insight into the dynamical details they did provide minimum potential energy configurations. From these configurations the various cluster properties, binding energy, rotational constants, dipole and quadrupole moments, were extracted. Verification of the

predicted geometries await new experiments to determine dipole moments, currently planned by the Brucat group.

Classical trajectories provide a method to simulate dynamic properties such as isomerization, rates of isomerization, radial distributions, and vibrational modes via FFT power spectra of the momenta of the clusters undergoing small excitation. The isomerization rates have given insight in to a relatively small system VAr_6^+ . The rates from modeling the intermediate behavior indicate that the first step from the **oct** complex to the intermediate is very important. This is true for both the canonical and microcanonical trajectory averages. The canonical trajectory averages give the k_{12} is more important while the microcanonical trajectory averages give the k_{21} is. At this point it is not clear if this behavior in the canonical trajectory averages is due to some artifact of The power spectra may prove to be the most useful aspect of the classical trajectory method, as it reveals modes which are not normally active in any conventional spectra.

All of these results together provide a relatively complete picture of transition metal ions interacting with solvent atom(s) or molecule(s). There are several projects which have not been taken to completion and could be with relative ease. The water systems need modeling of their rotational structure. The new values bond strengths and lengths for the diatomics investigated should allow for much more accurate modeling. They also provide better targets for theorists to hit. The static modeling here provides a general way to obtain geometries for larger systems. The dynamic modeling provides a method of obtaining modes of vibration not normally active. Combined, all of this makes a significant addition to what is known about diatomic and polyatomic cation systems.

APPENDIX COMPUTER CODES

Experimental Data Fitting Code

```
/* C++ Program to manage experimental data in the form of an x column and a y
 * column. The program takes various switches. The program compiles under OS/2
 * IBM's CSet++ 2.1 and DOS Borland C++ 3.1 or 4.0.
 * The functions which can be performed are listed if no switches or
 * parameters are given.
 *
 * Program Name:    <DatMan3.cpp> Ver 6.3 for C++
 * Author:         Robert L. Asher
 * Employer:       University of Florida / Philip J. Brucat
 * Original Date:   May 1, 1994
 * Revision Date:   Oct 30, 1994
 *
 */
```

```
#define NAME        "DatMan3.cpp"
#define DATE        "10/30/94"
#define VERSION     "6.3"
```

```
/****** Standard C++ Include Files
```

```
******/
```

```
#include <conio.h>           // C++ console routines
#include <ctype.h>           // C++ types
#include <fcntl.h>           // C++
#include <float.h>           // C++ floating point routines
#include <math.h>            // C++ math routines
#include <stddef.h>          // C++ standard definitions
#include <stdio.h>           // C++ standard I/O routines
#include <stdlib.h>          // C++ standard library
#include <stdarg.h>          // C++ standard argument
#include <string.h>          // C++ string routines
#include <iostream.h>        // C++ I/O stream routines
#include <fstream.h>         // C++ file I/O stream
#include <time.h>            // C++ time classes
```

```

#include <limits.h>

char In[80],Out[80];
long ibins,obins,i,j,Num;

#define ESIZE      (100000)      // make this smaller for Borland C++

float  Offset=0.0,
        Multiplier=1.0,
        Mass=1.0,
        Vmin=0.0,
        Vmax=0.0,
        Vres=0.2,
        Vdiff=0,
        W[5],
        V[5][100];

class XYData {
public:
    float x,y;
    XYData& operator=(const XYData&);
    XYData(float val) {x=y=val;};
    XYData() {x=y=0.0;};
} data[ESIZE], rdata[ESIZE];

XYData& XYData::operator=(const XYData& copy) {
    x=copy.x;
    y=copy.y;
    return *this;
}

/*****
*****/
void QuickSort(long left, long right) {
    i = left;
    j = right;
    register float test = data[(left + right) / 2].x;
    XYData swap;
    do {
        while (data[i].x < test) i++;
        while (test < data[j].x) j--;
        if (i <= j) {
            swap = data[i];

```

```

        data[i] = data[j];
        data[j] = swap;
        i++;
        j--;
    }
    } while (i <= j);
    if (left < j) QuickSort(left, j);
    if (i < right) QuickSort(i, right);
}

/*****
*****/
void Rebin(float Vmin,float Vmax, float Vres) {
    float l,h;
    double vert;
    long low,high,mid=0;

    if(Vmin==Vmax) { // incase there's no max and min just Vres
        Vmin=(float) ((long)data[0].x - 1);
        Vmax=(float) ((long)data[ibins-1].x + 1);
    }
    obins = (long)floor((double)(Vmax-Vmin)/Vres);
    if ((obins<0)|(obins>ESIZE)) {
        printf("\nerror in new frequency scale... exiting\n");
        exit(1);
    }
    for(j=0;j<obins;j++) {
        rdata[j].x = Vmin + (float)j*Vres;
        l = Vmin + ((float)j-0.5)*Vres;
        h = Vmin + ((float)j+0.5)*Vres;
        low=high=mid;
        while((data[low].x>l)&&(low>0)) low--;
        while((data[high].x<h)&&(high<ibins)) high++;
        mid=(low+high)/2;
        vert=0.0;
        for(i=low;i<high;i++)
            if((data[i].x>=l)&(data[i].x<h))
                if(fabs((double)data[i].y)>fabs(vert))
                    vert = (double)data[i].y;
        rdata[j].y=(float)vert;
    }
}

```



```

/*****
*****/
void SmartPeakPick(float Vmin,float Xres) {
    long k=0,check,low,high,nbins=ibins-1;
    float Height,Average,l,m,h;

    Average=data[0].y;
    for(i=1;i<ibins;i++) Average+=data[i].y;
    Average /= (float)obins;

    for(i=0;i<ibins;i++) {
        low=high=i;
        l = ((data[i].x-Xres)<data[0].x) ?
            data[0].x :
            data[i].x - Xres;
        h = ((data[i].x + Xres)>data[nbins].x) ?
            data[nbins].x :
            data[i].x + Xres;
        while((data[low].x>l)&&(low>0)) low--;
        while((data[high].x<h)&&(high<ibins)) high++;
        low++;
        high--;
        if((data[i-1].y<=data[i].y)&&(data[i].y>=data[i+1].y)) {
            check=1;
            for(j=low;j<high;j++)
                check *= (data[j].y<=data[i].y) ? 1 : 0;
            Height=(data[i].y-Average);
            check*=(Vmin<Height)?1:0;
            if(check) {
                rdata[k]=data[i];
                k++;
            }
        }
        }
    obins=k;
}

/*****
*****/
void PeakPick(float Vmin,long Num) {
    long k=0,check;
    float Height,Average;
    Average=data[0].y;

```

```

for(i=1;i<obins;i++) Average+=data[i].y;
Average /= (float)obins;
for(i=Num;i<obins-Num;i++) {
    if((data[i-1].y<=data[i].y)&&(data[i].y>=data[i+1].y)) {
        check=1;
        for(j=-Num;j<Num;j++)
            check *= (data[i+j].y<=data[i].y)?1:0;
        Height=(data[i].y-Average);
        check*=(Vmin<Height)?1:0;
        if(check) {
            rdata[k]=data[i];
            k++;
        }
    }
}
obins=k;
}

```

```

void Normalize(float Ynorm,float Yoff) {
    float Ymax,Ymin,Ydiff=0.0;

    Ymin=Ymax=data[0].y;
    for(i=1;i<obins;i++) {
        Ymax=(data[i].y>Ymax)?data[i].y:Ymax;
        Ymin=(data[i].y<Ymin)?data[i].y:Ymin;
    }
    Ydiff = Ymax-Ymin;
    for(i=0;i<obins;i++) {
        rdata[i].x=data[i].x;
        rdata[i].y((((data[i].y-Ymin)/Ydiff)*Ynorm)+Yoff;
    }
}

```

```

/*****
*****/
void FindProgression() {
    for(i=0;i<100;i++) {
        V[0][i]=(float)(i+1)*0.5;
        for(j=1;j<5;j++) V[j][i]=V[j-1][i]*V[0][i];
    }
}

```

```

/*****
*****/
void Smooth(long Num) {
    obins=ibins-Num+1;
    XYData Zero(0.0);
    float *Mult,val,Pi;
    Pi=4.0*atan(1.0);
    Mult = new float[Num];
    for(i=0;i<Num;i++) {
        val = (float)(i+1)*Pi/(float)(Num+1);
        Mult[i]=sin(val);
        Mult[i]*=Mult[i];
        Mult[i]/=2.0;
    }
    for(i=0;i<obins;i++) {
        rdata[i]=Zero;
        for(j=0;j<Num;j++) {
            rdata[i].x+=data[i+j].x;
            rdata[i].y+=Mult[j]*data[i+j].y;
        }
        rdata[i].x/=(float)Num;
    }
}

/*****
*****/
int FileOut(char *fnam,char it) {
    int err=0;
    FILE *File;
    if((File = fopen(fnam,"a")) == NULL) {
        printf("\nUNABLE TO CREATE FILE <%s>",fnam);
        err=1;
    }
    else {
        printf("\nbins count out file = %5u\n",obins);
        switch(it) {
            case 'p':
            case 'q':
            case 'r':
            case 'R':
            case 's':
            case 'Y':
                for(i=0;i<obins;i++)

```

```

        if (rdata[i].y>(float)((long)rdata[i].y))
            fprintf(File,"%0.2f %0f\n",
                    rdata[i].x,rdata[i].y);
        else
            fprintf(File,"%0.2f %0f\n",
                    rdata[i].x,rdata[i].y);
        break;
case 'c':
    for(i=0;i<obins;i++) if((data[i].x>Vmin)&&(data[i].x<Vmax)) {
        if (data[i].y>(float)((long)data[i].y))
            fprintf(File,"%0.2f %0f\n",
                    data[i].x,data[i].y);
        else
            fprintf(File,"%0.2f %0f\n",
                    data[i].x,data[i].y);
    }
    break;
case 'P':
case 'Q':
case 'I':
    for(i=0;i<obins;i++)
        if (rdata[i].y>(float)((long)rdata[i].y))
            fprintf(File,"%0.2f %0d\n%0.2f %0f\n%0.2f %0d\n",
                    rdata[i].x,0,
                    rdata[i].x,rdata[i].y,
                    rdata[i].x,0);
        else
            fprintf(File,"%0.2f %0d\n%0.2f %0f\n%0.2f %0d\n",
                    rdata[i].x,0,
                    rdata[i].x,rdata[i].y,
                    rdata[i].x,0);

    break;
default:
    for(i=0;i<obins;i++)
        if (data[i].y>(float)((long)data[i].y))
            fprintf(File,"%0.2f %0f\n",
                    data[i].x,data[i].y);
        else
            fprintf(File,"%0.2f %0f\n",
                    data[i].x,data[i].y);

    break;
}
}

```

```

        fclose(File);

        return(err);
    }

    /**
    *****/
int FileIn(char *fnam) {
    int err=0;
    double d1,d2;
    char cbuf[120],cdum[120],c;
    FILE *File;
    if((File = fopen(fnam,"r")) == NULL) {
        printf("\nUNABLE TO OPEN FILE <%s>",fnam);
        err=1;
    } else {
        for(ibins=0;((fscanf(File,"%[^\\n]\\n",cdum) != EOF)
            & (ibins<ESIZE)); ibins++) {
            if(!strnicmp(cdum,"end",3)) {
                printf("\nend line found");
                break;
            }
            sscanf(cdum,"%lf%lf",&d1,&d2);
            data[ibins].x=(float)d1;
            data[ibins].y=(float)d2;
        }
        printf("\nbin count found in file = %5u\\n",ibins);
    }
    fclose(File);
    return(err);
}

    /**
    *****/
int main(int argc,char **argv) {
    int error=0;
    char What='0';
    printf("\n%s %s V%s Revised %s \\trla %d\\n",
        argv[0],NAME,VERSION,DATE,argc);
    if((argc==3)&&(argv[1][0]!='/')) {
        strcpy(In,argv[1]);
        strcpy(Out,argv[2]);
        error=FileIn(In);
    }
}

```



```

    obins=ibins;
    if(!error&&obins>1) QuickSort(0,obins-1);
} else if((argc>=3)&&(argv[1][0]!='/')) {
    What=argv[1][1];
    strcpy(In,argv[2]);
    if (argc>3) strcpy(Out,argv[3]);
    error=FileIn(In);
    obins=ibins;
    if(!error&&obins>1) QuickSort(0,obins-1);
    if(!error) switch(What) {
    case 'd':          // Doppler shift x data.
        if(argc>4) {
            Mass=atof(argv[4]);
            Multiplier=1.0+(1.3891*sqrt(1450.0/Mass)/29979.2458);
            for(i=0;i<obins;i++) data[i].x*=Multiplier;
        } else error=1;
        break;
    case 'c':          // Sort but cut at Vmin and Vmax.
        if(argc>5) {
            Vmin=atof(argv[4]);
            Vmax=atof(argv[5]);
        } else error=1;
        break;
    case 'l':          // Generate equal intensity line list.
        if(argc>4) {
            Offset=atof(argv[4]);
            for(i=0;i<obins;i++) data[i].y=Offset;
        }
        for(i=0;i<obins;i++) rdata[i]=data[i];
        break;
    case 'm':          // give max and min Y values
        Vmin=Vmax=data[0].y;
        for(i=1;i<obins;i++) {
            Vmax=(data[i].y>Vmax)?data[i].y:Vmax;
            Vmin=(data[i].y<Vmin)?data[i].y:Vmin;
        }
        Vdiff = Vmax-Vmin;
        printf("max: %f\nmin: %f\ndiff: %f\n",Vmax,Vmin,Vdiff);
        break;
    case 'P':
    case 'p':          // Peak simple picking routine.
        if(argc>5) {
            Vmin=atof(argv[4]);

```

```

        Num=atol(argv[5]);
        PeakPick(Vmin,Num);
    } else error=1;
    break;
case 'Q':
case 'q':        // Peak simple picking routine.
    if(argc>5) {
        Vmin=atof(argv[4]);
        Vres=atof(argv[5]);
        SmartPeakPick(Vmin,Vres);
    } else error=1;
    break;
case 'R':        // Rebin using Vres default to find Vmin Vmax
    if(argc>4) {
        Vres=atof(argv[4]);
        Rebin(0.0,0.0,Vres);
    } else error=1;
    break;
case 'r':        // Rebin the Data using Vmin, Vmax and Vres.
    if(argc>6) {
        Vmin=atof(argv[4]);
        Vmax=atof(argv[5]);
        Vres=atof(argv[6]);
        Rebin(Vmin,Vmax,Vres);
    } else error=1;
    break;
case 's':
    if(argc>4) {
        Num=atol(argv[4]);
        if(Num%2) Smooth(Num);
        else error=2;
    } else error=1;
    break;
case 'x':        // X mult and offset
    if(argc>5) {
        Multiplier=atof(argv[4]);
        Offset=atof(argv[5]);
        for(i=0;i<obins;i++) {
            data[i].x*=Multiplier;
            data[i].x+=Offset;
        }
    } else error=1;
    break;

```

```

case 'y':      // Y mult and offset
    if(argc>5) {
        Multiplier=atof(argv[4]);
        Offset=atof(argv[5]);
        for(i=0;i<obins;i++) {
            data[i].y*=Multiplier;
            data[i].y+=Offset;
        }
    } else error=1;
    break;
case 'Y':      /* Y normalize and offset */
    if(argc>5) {
        Multiplier=atof(argv[4]);
        Offset=atof(argv[5]);
        Normalize(Multiplier,Offset);
    } else error=1;
    break;
case 'w':      // attempt to find Te0, We, WeXe, ...
    if(argc>6) {
        Vmin=atof(argv[4]);
        Num=atol(argv[5]);
        W[1]=atof(argv[6]); // We 1st try
        PeakPick(Vmin,Num);
        FindProgression();
    } else error=1;
    break;
default:
    printf("\nIncorrect switch, use:");
    printf("\n/c /d /l /m /p /P /q /Q /r /R /s /w /x /y /Y.");
    error=2;
    break;
}
} else {
    printf("\n%s Correct Syntax:      ",argv[0]);
    printf("Where In and Out are file names.");
    printf("\n%s In Out      ",argv[0]);
    printf("No switch for simple sort.");
    printf("\n%s /c In Out Xmin Xmax      ",argv[0]);
    printf("/c sorts but cuts of at Xmin and Xmax.");
    printf("\n%s /d In Out Mass      ",argv[0]);
    printf("/d doppler shift x data.");
    printf("\n%s /l In Out Intensity      ",argv[0]);
    printf("/l add 0's to a line list for displaying.");

```

```

printf("\n%s /m In          ",argv[0]);
printf("/m give max and min y values.");
printf("\n%s /p In Out Ymin N          ",argv[0]);
printf("/p peakpick y data using Ymin by N-points.");
printf("\n%s /P In Out Ymin N          ",argv[0]);
printf("/P same as /p but puts in 0's like /l.");
printf("\n%s /q In Out Ymin Xres      ",argv[0]);
printf("/q same as /p but uses Ymin and Xres.");
printf("\n%s /Q In Out Ymin Xres      ",argv[0]);
printf("/Q same as /P but uses Ymin and Xres.");
printf("\n%s /r In Out Xmin Xmax Xres ",argv[0]);
printf("/r rebins from Xmin to Xmax by Xres.");
printf("\n%s /R In Out Xres          ",argv[0]);
printf("/R rebins smallest to largest by Xres.");
printf("\n%s /s In Out N          ",argv[0]);
printf("/s smooth with odd-N-point smooth.");
printf("\n%s /w In Out          ",argv[0]);
printf("/w finds progressions in We, WeXe.");
printf("\n%s /x In Out Mult Off      ",argv[0]);
printf("/x multiplies and shifts x.");
printf("\n%s /y In Out Mult Off      ",argv[0]);
printf("/y multiplies and shifts y.");
printf("\n%s /Y In Out Norm Off      ",argv[0]);
printf("/Y normalizes and shifts y.");
exit(1);
}
if((!error)&&(What!='m')) error=FileOut(Out,What);
if(error) printf("\nUnresolved Error # %d",error);
else printf("\ndone.");
return(error);
}

```

Rotational Spectra Fitting Code

```
/* C Program to manage rotational experimental data in the form of an x column and a y
 * column. The program operates manually and is compiled under microsoft C 5.1.
 *
```

```
* Program Name:    <p5Krla.c> Ver 3 for C
* Author:          Robert L. Asher / Philip J. Brucat
* Employer:        University of Florida / Philip J. Brucat
* Original Date:    May 1, 1994
* Revision Date:    Nov 8, 1994
*/
```

```
#define LINT_ARGS
#include <pjb.h>
#define HEADLN "<0.5K> Spectrum Simulator whole integral J,K 11/8/94 /pjb/rla\n"
#define graphmode() _setvideomode(16)          /* 640 X 350 */
#define textmode()  _setvideomode(_DEFAULTMODE)
#define cls()       _clearscreen(_GCLEARSCREEN)
#define locate(a,b) _settextposition(a+1,b+1)
#define HRES        512
#define LEFT        64
#define RIGHT        576
#define TOP          60.0
#define BOT          290.0
#define TOPBOT       -230.0                    /* TOP minus BOT */
#define OVERSIZE     1.2
#define CCUTOFF       1e-5
#define KLOWER        0.5                    /* 0.0 normal, 0.5 half integral */
#define TICKLEN       5.0
#define SNUM          1000
#define ESIZE         8000
#define ICUTOFF        1e-3
#define TICK_COLOR    15
#define BOX_COLOR      8
#define CURVE_COLOR    14
#define ESIG_COLOR     13
#define BOX_TEXT_COLOR 7
#define P_COLOR        12
#define Q_COLOR        10
#define R_COLOR        9

char vt[120];
```



```

double      v=17946.0,
            Bup= 0.6,
            Blow=0.56, /* B=0.292 C=0.286*/
            Bifact=1.083,
            Dup=1e-100,
            Dlow=1e-100,
            Dinc=1e-100,
            kT=10.0,
            hot_ratio=1.0,
            hot_frac=0.05,
            res=0.005,
            lockv,
            targetlock,

            esigmax,
            svmin,svmax,imax,
            cmax,
            vmin,vmax, /* manual horizontal scaling factor for plot */
            Binc=0.001,
            kTinc=1.1,
            iscale=1.2,
            Klower=KLOWER,
            Jmax=30,
            Kmax=8,
            Jlock=(5.0+KLOWER);

char         fnam[80];
char         enam[80];

int          draw_curve=0,both=0,draw_esig=0,
            delJlock=1,
            linelock,
            deltaK=1,
            lock=0,
            max=1,
            ebins=0,
            page=0,
            v_manual=0,
            sticknum=0; /* running index of sticklist[] */

double far plotdata[HRES],lineshape[HRES];
double far sticklist[3][SNUM];
float far transitions[4][SNUM];

```

```

double huge esig[2][ESIZE];
double huge csig[2][ESIZE];
/*****
*****/
double line_frequency(int delJ, double J) { /* J=J" */
    double dum;
    dum = v + Bup*(J+delJ)*(J+delJ+1)
        - Dup*(J+delJ)*(J+delJ)*(J+delJ+1)*(J+delJ+1);
    dum -= (Blow*J*(J+1) - Dlow*J*J*(J+1)*(J+1));
    return(dum);
}

/*****
*****/
double HL_fact(int delJ, int delK, double J, double K) { /* J=J" K=K" */
    double dum;
    switch(delJ) {
    case 1:
        switch(delK) {
        case 0: dum = (double)(J+1+K)*(J+1-K)/(J+1);break;
        case 1: dum = (double)(J+2+K)*(J+1+K)/(4*(J+1));break;
        case -1: dum = (double)(J+2-K)*(J+1-K)/(4*(J+1));break;
        }
        break;
    case 0:
        switch(delK) {
        case 0: dum = (double)(2*J+1)*K*K/(J*(J+1));break;
        case 1: dum = (double)(J+1+K)*(J-K)*(2*J+1)/(4*J*(J+1));break;
        case -1: dum = (double)(J+1-K)*(J+K)*(2*J+1)/(4*J*(J+1));break;
        }
        break;
    case -1:
        switch(delK) {
        case 0: dum = (double)(J+K)*(J-K)/J;break;
        case 1: dum = (double)(J-1-K)*(J-K)/(4*J);break;
        case -1: dum = (double)(J-1+K)*(J+K)/(4*J);break;
        }
        break;
    }
    return(dum);
}

```

```

/*****
*****/
double Boltz_fact(double J, double K) {
    double dum,ret;
    dum = -(Blow*J*(J+1))/kT;
    ret = (1.0-hot_frac)*exp(dum);
    dum = -(Blow*J*(J+1)*hot_ratio)/kT;
    dum = exp(dum);
    dum *= hot_frac;
    ret += dum;
    return(ret);
}

/*****
*****/
void clear_plotdata() {
    int i;
    for(i=0;i<HRES;i++) plotdata[i] = 0.0;
    for(i=0;i<SNUM;i++)
        sticklist[0][i] = sticklist[1][i] = sticklist[2][i] = 0.0;
    sticknum=0;
}

/*****
*****/
void add_line(double vline, double iline, int delJ,
              double J,int delK,double Klow) {

    sticklist[0][sticknum] = vline;
    sticklist[1][sticknum] = iline;
    switch(delJ) {
    case -1: sticklist[2][sticknum] = P_COLOR; break;
    case 0: sticklist[2][sticknum] = Q_COLOR; break;
    case 1: sticklist[2][sticknum] = R_COLOR; break;
    }
    transitions[0][sticknum]=(float far)J;
    transitions[1][sticknum]=(float far)(J+delJ);
    transitions[2][sticknum]=(float far)Klow;
    transitions[3][sticknum]=(float far)(Klow+delK);
    if((J==Jlock)&&(delJ==delJlock)) {
        linelock=sticknum;
        lockv=sticklist[0][sticknum];
    }
}

```

```

sticknum++;
if(sticknum>=SNUM) {
    locate(10,20);
    printf("MEMORY OVERFLOW ...");
    getch();
    printf("\n\n\t\tYou should exit now");
    getch();
}
}

/*****
*****/
void stick_spectrum() {
    int delJ,delK;
    double J,Klow;
    double vline,iline;
    delK=deltaK;
    Klow=Klower;
    if((Klow+delK)>=0)
    for(J=Klow;J<=Jmax;J++)
        for(delJ=-1;delJ<=1;delJ++)
            if((J+delJ)>=(Klow+delK))
                if(delJ || delK || (Klow!=0.0)) {
                    vline = line_frequency(delJ,J);
                    iline = HL_fact(delJ,delK,J,Klow);
                    iline *= Boltz_fact(J,Klow);
                    add_line(vline,iline,delJ,J,delK,Klow);
                }
}

/***** Generate instrument lineshape function *****/
void gen_lineshape() {
    int i;
    double dum,df;
    df = (vmax-vmin)/HRES;
    max =(int)floor(-(res/(df*df))*log(CCUTOFF));
    if(max<1) max=1;
    if(max>HRES) max=HRES;
    for(i=0;i<max;i++) {
        dum = i*df;
        dum = -(dum*dum)/res;
        lineshape[i] = exp(dum);
    }
}

```

```

        for(i=max;i<HRES;i++) lineshape[i]=0.0;
    }

/*****
*****/
void add_lineshape(int cent, double iline) {
    int j,jj;
    jj=cent+max;
    if(jj>HRES) jj=HRES;
    for(j=cent;j<jj;j++) if(j>=0) plotdata[j]+=iline*lineshape[j-cent];
    jj=cent-max;
    if(jj<0) jj=0;
    for(j=cent-1;j>=jj;j--)
        if(j<HRES) plotdata[j]+=iline*lineshape[cent-j];
}

/*****
*****/
void contour() {
    int i,icent;
    double cent,df,p0,p1,dum;
    df=(vmax-vmin)/((double)HRES);
    for(i=0;i<sticknum;i++) {
        dum=(sticklist[0][i]-vmin)/df;
        cent=floor(dum);
        icent=(int)cent;
        p1=dum-cent;
        p0=1.0-p1;
        add_lineshape(icent,p0*sticklist[1][i]);
        add_lineshape((icent+1),p1*sticklist[1][i]);
    }
}

/*****
*****/
void cscale() {
    int i;
    cmax=plotdata[0];
    for(i=1;i<HRES;i++) if(cmax<plotdata[i]) cmax=plotdata[i];
}

/*****
*****/

```



```

void sscale() {
    int st,fl=1;
    imax=sticklist[1][0];
    for(st=0;st<sticknum;st++)
        imax=(imax<sticklist[1][st])?sticklist[1][st]:imax;
    for(st=0;st<sticknum;st++) if (sticklist[1][st]>imax*ICUTOFF) {
        if(fl) {
            fl=0;
            svmin=svmax=sticklist[0][st];
        }
        svmin=(svmin>sticklist[0][st])?sticklist[0][st]:svmin;
        svmax=(svmax<sticklist[0][st])?sticklist[0][st]:svmax;
    }
    svmax=(0.55)*(svmax-svmin)+(0.5)*(svmax+svmin);
    svmin=(-0.55)*(svmax-svmin)+(0.5)*(svmax+svmin);
}

/*****EXPERIMENTAL DATA ARRAY FILE
INPUT*****/
void fread_esig() {
    FILE *dfile;
    double frq,dis;
    int i;
    dfile = fopen(enam,"r");
    if(dfile==NULL) return;
    for(ebins=0;
        ((fscanf(dfile," %lf %lf\n",&frq,&dis) != EOF) && (ebins<ESIZE));
        ebins++) { esig[0][ebins]=frq;esig[1][ebins]=dis;}
    fclose(dfile);
    esigmax=esig[1][0];
    for(i=0;i<ebins;i++)
        if (esig[1][i] > esigmax) esigmax=esig[1][i];
}

void dump_list() {
    FILE *dumpfile;
    char fnam[80];
    int i;
    double Jup,Jlow,Kup,Klow;
    double frq,dss;
    do {
        locate(7,10);printf("%50s"," ");
        locate(7,10);printf("Parameter file to output?: ");
    }

```

```

        skeyin(fnam);
        dumpfile = fopen(fnam,"a+");
    } while(dumpfile == NULL);
    fprintf(dumpfile,HEADLN);
    fprintf(dumpfile,"\nBup: %lf\nBlow: %lf\nv: %lf\nkT: %lf\n",
        Bup,Blow,v,kT);
    fprintf(dumpfile,"\n\n%10s%10s%10s%10s%15s%15s\n",
        "Kupper","Klower","Jupper","Jlower","frequency","intensity");
    for(i=0;i<sticknum;i++) {
        Kup=(double)transitions[3][i];
        Klow=(double)transitions[2][i];
        Jup=(double)transitions[1][i];
        Jlow=(double)transitions[0][i];
        fprintf(dumpfile,"\n%10.1lf%10.1lf%10.1lf%10.1lf",
            Kup,Klow,Jup,Jlow);
        frq=sticklist[0][i];
        dss=sticklist[1][i];
        fprintf(dumpfile,"%15.2lf%15lf",frq,dss);
    }
    fprintf(dumpfile,"\n\n");
    fclose(dumpfile);
}

void esig_shift(double a) {
    int i;
    for(i=0;i<ebins;i++) esig[1][i] += a;
}

/***** PLOTTING ROUTINES *****/
void plot_esig() {
    int i,x,y,onscale=0;
    double ehscale;
    if(!ebins) return;
    if(esigmax==0.0) return;
    _setcolor(ESIG_COLOR);
    ehscale = (vmax-vmin);
    y = (int)(BOT + TOPBOT*(esig[1][0]/(esigmax*iscale)));
    if (y<TOP) y=TOP;
    if (y>BOT) y=BOT;
    x = (int)(LEFT+ HRES*((esig[0][0]-vmin)/ehscale));
    if ((x>=LEFT)&&(x<HRES+LEFT)) {
        _moveto(x,y);
    }
}

```

```

        onscale=1;
    }
    for(i=1;i<ebins;i++) {
        y = (int)(BOT + TOPBOT*((esig[1][i])/(esigmax*iscale)));
        if (y<TOP) y=TOP;
        if (y>BOT) y=BOT;
        x = (int)(LEFT + HRES*((esig[0][i]-vmin)/ehscale));
        if((x>=LEFT)&&(x<HRES+LEFT)) {
            if(onscale) {_lineto(x,y);}
            else {_moveto(x,y);onscale=1;}
        } else {onscale=0;}
    }
}

void dump_contour() {
    int i;
    FILE *dumpfile;
    char fnam[80];
    double frq,dss,vres;
    vres=(vmax-vmin)/(double)HRES;
    contour();
    do {
        locate(7,10);printf("%50s", " ");
        locate(7,10);printf("Contour file to output?: ");
        skeyin(fnam);
        dumpfile = fopen(fnam,"a+");
    } while(dumpfile == NULL);
    for(i=0;i<HRES;i++) {
        dss = 1000.0 * plotdata[i];
        frq = vmin + vres * (double)i;
        fprintf(dumpfile,"%0.6lf %0.6lf\n",frq,dss);
    }
    for(i=0;i<sticknum;i++) {
        frq = sticklist[0][i];
        dss = 1000.0 * sticklist[1][i];
        if((frq>=vmin)&&(frq<=vmax))
            fprintf(dumpfile,"%0.6lf 0\n%0.6lf %0.6lf\n%0.6lf 0\n",
                    frq,frq,dss,frq);
    }
    fclose(dumpfile);
}

void plot_curve() {

```

```

int i,x,y;
if(yscale*cmax==0.0) return;
_setcolor(CURVE_COLOR);
y = BOT + TOPBOT*plotdata[0]/(yscale*cmax);
if (y<TOP) y=TOP;

_moveto(LEFT,y);

for(i=1;i<HRES;i++) {
    y = (int)(BOT + TOPBOT*plotdata[i]/(yscale*cmax));
    if (y<TOP) y=TOP;
    _lineto(LEFT+i-1,y);
}
}

void sticker() {
    int i,x,y;
    if(yscale==0.0) return;
    for(i=0;i<sticknum;i++) {
        if(i==linelock) {
            if(lock) {
                _setcolor(15);
            } else { _setcolor(7); }
        }
        else _setcolor((int)sticklist[2][i]);
        x= LEFT+(int)((double)HRES*(sticklist[0][i]-vmin)/(vmax-vmin));
        y = BOT + TOPBOT*(sticklist[1][i]/imax)/yscale;
        if(y<TOP) y=TOP;
        if ((x>LEFT)&&(x<RIGHT)) {
            _moveto(x,BOT);
            _lineto(x,y);
        }
    }
}

void box_text() {
    char branch;
    switch(delJlock) {
        case 0: branch = 'Q';break;
        case 1: branch = 'R';break;
        case -1: branch = 'P';break;
    }
    _settextcolor(BOX_TEXT_COLOR);
    locate(0,0);sprintf(vt,HEADLN);_outtext(vt);
}

```

```

locate(1,5);sprintf(vt,"v= %9.2lf",v);_outtext(vt);
locate(2,5);
sprintf(vt,"Klow=%2.1lf delK=%2d",Klower,deltaK);_outtext(vt);
locate(3,5);
sprintf(vt,"%c(%2.1lf) = %9.2lf",branch,Jlock,lockv);_outtext(vt);

```

```

locate(1,30);sprintf(vt,"B'=%8.4lf",Bup);_outtext(vt);
locate(2,30);sprintf(vt,"B\"=%8.4lf",Blow);_outtext(vt);
locate(1,48);sprintf(vt,"D\"=%10.2le",Dlow);_outtext(vt);
locate(2,48);sprintf(vt,"D'=%10.2le",Dup);_outtext(vt);
if(!v_manual){locate(23,12);sprintf(vt,"auto scale");_outtext(vt);}
if(lock){locate(22,12);sprintf(vt,"line lock");_outtext(vt);}
locate(3,30);
sprintf(vt,"kT=%4.1lf & %4.1lf",kT,kT/hot_ratio);_outtext(vt);
locate(3,48);sprintf(vt,"file: %s",enam);_outtext(vt);
locate(21,3);sprintf(vt,"%7.0lf",vmin);_outtext(vt);
locate(21,68);sprintf(vt,"%7.0lf",vmax);_outtext(vt);

```

```

}

```

```

void box() {
    int xt,tick,low,yt,high;
    low = (int)vmin;
    if((double)low<vmin) low++;
    high = (int)vmax;
    if((double)high>vmax) high--;
    _setcolor(BOX_COLOR);
    _moveto(LEFT,(int)BOT);
    _lineto(LEFT,(int)TOP);
    _lineto(RIGHT,(int)TOP);
    _lineto(RIGHT,(int)BOT);
    _lineto(LEFT,(int)BOT);
    _setcolor(TICK_COLOR);
    xt = LEFT+(int)(HRES*(v-vmin)/(vmax-vmin));
    _moveto(xt,BOT+3*TICKLEN);
    _lineto(xt,BOT);
    _moveto(xt+1,BOT+3*TICKLEN);
    _lineto(xt+1,BOT+2*TICKLEN);
    _moveto(xt-1,BOT+3*TICKLEN);
    _lineto(xt-1,BOT+2*TICKLEN);
    for(tick=low;tick<=high;tick++) {
        xt = LEFT+(int)(HRES*((double)tick-vmin)/(vmax-vmin));
        _moveto(xt,(int)BOT);
        if(!(tick%10)) yt=BOT+2*TICKLEN;
    }
}

```



```

        else yt=BOT+TICKLEN;
        if(!(tick%2)||((vmax-vmin)<50.0)) {_lineto(xt,yt);}
    }
    box_text();
}

void black_on_white() {
    int i;
    for(i=1;i<16;i++) _remappalette(i,_BLACK);
    _remappalette(0,_BRIGHTWHITE);
}

void blue_backround() {
    _remappalette(0,_BLUE);
    _remappalette(8,_WHITE);
    _remappalette(7,_BROWN);
}

/***** END PLOTTING *****/
void rot_constants() {
    double temp;
    locate(6,10);
    printf("\n\tinput band origin[%5lf cm^-1]: ",v);
    if ((temp=inf()) > 0.0) v = temp;
    printf("\n\tinput B\" [%10.6lf cm^-1]: ",Blow);
    if ((temp=inf()) > 0.0) Blow = temp;
    printf("\n\tinput B' [%10.6lf cm^-1]: ",Bup);
    if ((temp=inf()) > 0.0) Bup = temp;
    printf("\n\tinput D\" [%10.2le cm^-1]: ",Dlow);
    if ((temp=inf()) > 0.0) Dlow = temp;
    printf("\n\tinput D' [%10.2le cm^-1]: ",Dup);
    if ((temp=inf()) > 0.0) Dup = temp;
    printf("\n\tinput rotational energy kT [%6.2lf cm^-1]: ",kT);
    if ((temp=inf()) > 0.0) kT = temp;
    printf("\n\tinput fraction of 'hot' molecules[%6.3lf]: ",hot_frac);
    temp=inf();
    if ((temp > 0.0)&&(temp<1.0)) hot_frac=temp;
    printf("\n\tinput hot/normal temperature ratio[%6.1lf]: ",
        1.0/hot_ratio);
    if ((temp=inf()) > 0.0) hot_ratio=1.0/temp;
}

```

```

void increments() {
    double temp;
    locate(6,10);
    printf("\n\tinstrument resolution squared[%8.4lf cm^-1]: ",res);
    if ((temp=inf()) != 0) {res = temp;gen_lineshape();}
    printf("\n\tincrement for B rotational constants [%8.4le cm^-1]: ",
        Binc);
    if ((temp=inf()) != 0) Binc=temp;
    printf("\n\tincrement for D rotational constants [%8.4le cm^-1]: ",
        Dinc);
    if ((temp=inf()) != 0) Dinc=temp;
    printf("\n\tmaximum J to be calculated [%5d]: ",Jmax);
    if ((temp=inf()) != 0) Jmax=(int)temp;
}

```

```

void menu(char c) {
    char d;
    double temp;
    switch(c) {
    case '+':esig_shift(esigmax*iscale/8.0);break;
    case '-':esig_shift(-esigmax*iscale/8.0);break;
    case 'K':Klower++; break;
    case 'k':Klower--; if(Klower<0) Klower=KLOWER;
        if((deltaK+Klower)<0) Klower = KLOWER-deltaK;
        break;
    case 'P':deltaK--; if(deltaK<-1) deltaK=1;
        if(Klower+deltaK<0) Klower=KLOWER-deltaK; break;
    case 'a':v_manual^=1;break;
    case 'i':draw_esig=1;
        locate(7,10);printf("%50s", " ");
        locate(7,10);printf("Experimental data file for input?: ");
        skeyin(enam);
        fread_esig();break;
    case 'T':draw_esig^=1;break;
    case 'o':dump_list();break;
    case 'O':dump_contour();break;
    case 'b':both^=1;break;
    case ',':Bup+=5.0*Binc;Blow+=5.0*Binc;break;
    case '.':Bup-=5.0*Binc;Blow-=5.0*Binc;
        if(Bup<=0.0) Bup=Binc; if(Blow<=0.0) Blow=Binc;
        break;
    case '<':esigmax *= 1.2;break;
    case '>':esigmax /= 1.2;break;

```

```

case 'c':draw_curve^=1; break;
case 'n':Dup-=Dinc;break;
case 'N':Dup+=Dinc;break;
case 'M':Dlow+=Dinc;break;
case 'm':Dlow-=Dinc;break;
case 'U':Bup+=Binc; break;
case 'u':Bup-=Binc; if(Bup<=0.0) Bup=Binc; break;
case 'v':v-=(vmax-vmin)/64.0; break;
case 'V':v+=(vmax-vmin)/64.0; break;
case 'w':black_on_white();break;
case 'W':blue_background();break;
case 'L':Blow+=Binc; break;
case 'l':Blow-=Binc; if(Blow<=0.0) Blow=Binc; break;
case 'T':kT*=kTinc;break;
case 't':kT/=kTinc;break;
case 'r':rot_constants();break;
case 'R':increments();break;
case 'J':delJlock++;if(delJlock>1){delJlock=-1;Jlock++;}break;
case 'j':delJlock--;if(delJlock<-1){delJlock=1;Jlock--;}break;
case 'x':lock^=1;if(lock)targetlock=lockv;break;
case 'A':v_manual=1;
    locate(6,10);
    printf("lower frequency limit (%12.2lf)?: ",vmin);
    if ((temp=inf()) != 0) vmin = temp;
    locate(7,10);
    printf("upper frequency limit (%12.2lf)?: ",vmax);
    if ((temp=inf()) != 0) vmax = temp;
    gen_lineshape();
    break;
case 'y':locate(6,10);printf("vertical scale (%6.2lf)?:",iscale);
    temp=inf(); if(temp>0.0) iscale=temp; break;
case 0: d=getch();
    temp=vmax-vmin;
    switch(d) {
    case 72:iscale /= 1.2; break;
    case 80:iscale *= 1.2; break;
    case 116:vmin -= (temp/8.0);
        vmax -= (temp/8.0);
        break;
    case 115:vmin += (temp/8.0);
        vmax += (temp/8.0);
        break;
    case 75:

```

```

        {vmax+=(temp/3.0);}
        gen_lineshape();
        break;
    case 77:
        {vmax-=(temp/4.0);}
        gen_lineshape();
        break;
    }
    break;
}
}

```

```

void spec_display() {
    clear_plotdata();
    stick_spectrum();
    if(lock) {
        v-=(lockv-targetlock);
        clear_plotdata();
        stick_spectrum();
    }
    sscale();
    if(!v_manual) {
        vmin=svmin;
        vmax=svmax;
        gen_lineshape();
        iscale=1.2;
    }
    page ^=1;
    _setactivepage(page);
    cls();
    box();
    if(draw_esig) plot_esig();
    if(draw_curve) {
        contour();
        cscale();
        plot_curve();
        if(both) sticker();
    } else sticker();
    _setvisualpage(page);
}

```

```

int main(int argc,char **argv) {
    char c;

```

```
if(argc>=2) {
    strcpy(enam,argv[1]);
    fread_esig();
    draw_esig=1;
}
graphmode();
printf(HEADLN);
do {
    spec_display();
    while (kbhit()) getch();
    c=getch();
    menu(c);
} while (c!='q');
textmode();
return(0);
}
→
```


Simulated Annealing Code

```

/*
 * 11/20/94 Robert L. Asher - University of Florida
 *
 * Optimization of MX(n) using Simulated Annealing method eventually want to
 * use gradient driven minimization in the neighborhood of a local minima.
 * Can use any potentials provided they use the parameters set up in
 * "pot.h" the potentials reside in "pot.c" and the parameter assignments
 * are as well. Presently the program can use 8 - 4 potentials
 * or Morse-switch-4 for MS interactions and Morse spline van der Waals or
 * Lennard Jones 12 - 6 for SS interactions. And a 3 body potential due
 * to the interaction of induced dipoles.
 */

/***** Standard Include Files
*****/
#include <stdio.h>
#include <stdlib.h>
#include <string.h>
#include <math.h>
#include <values.h>
#include <ctype.h>
#include <time.h>

#define PI      (3.14159265359)
#define H      (6.626176e-34)          /* planks const (J.s)          */
#define H2     ((H)*(H))
#define HBAR   ((H)/(2*PI))
#define HBAR2  ((HBAR)*(HBAR))
#define HPLANK (6.6256e-27)           /* planks const (erg)          */
#define C      (299792458.0)          /* speed of light (m/s)        */
#define CSPEED (2.997925e10)          /* speed of light (cm/s)       */
#define Na     (6.022045e23)          /* avagadros #                  */
#define Qe     (1.6021892e-19)        /* charge on electr (C)         */
#define Qe2    ((Qe)*(Qe))
#define Qe4    ((Qe2)*(Qe2))
#define Kb     (1.380662e-23)          /* boltzmann const (J/K)        */
#define KBOLTZ (1.38054e-16)          /* boltzmann const (erg/K)      */
#define Me     (9.109534e-31)          /* mass of electron (kg)        */
#define G      (6.672e-11)             /* universal gavitational const */
#define AMU    (1.6605655e-27)        /* 1 amu (kg)                   */

```

```

#define EPO  (8.854187818e-12) /* permitivity free space (F/m) */
#define K  ((4)*(PI)*(EPO))
#define MUO  (1.256637061e-6) /* mag permitiv f s (H/m) */
#define Mp  (1.67265e-27) /* mass proton (kg) */
#define Mn  (1.67495e-27) /* mass neutron (kg) */
#define F  ((Qe)*(Na)) /* faraday's const */
#define MUB  (((Qe)*(HBAR))/((2.0)*(Me))) /* bohr magneton */
#define MUN  (Qe*HBAR)/(2.0*Mp) /* nuclear magneton */
#define HYPFINE  (MUO*Qe2*C)/(2.0*H) /* fine struct constant */
#define AO  (K*HBAR2)/(Me*Qe2) /* bohr radius */
#define QeSTAT  ((Qe)*(C)*(10))
#define QeSTAT2  (QeSTAT*QeSTAT)
#define ROTCON  ((H)/(8.0*PI*PI*C*100.0))

/***** CONVERSION CONSTANTS *****/

#define ANGST  (1e-10) /* langstrom = 10-10 m */
#define HARTREE  (Qe4*Me)/(4*H2*EPO*EPO) /* 1hartree = #10-18 J */
#define KCAL  (4186.05/Na) /* 1kcal/mole = #10-21 J */
#define eV  (Qe) /* 1eV=Qe J */
#define ERG  (1e-7) /* 1erg=10-7 J */
#define CM1  (100.0*C*H) /* 1cm-1= #10-23 J */
#define EV2CM  (8065.5) /* 1eV = 8065.5 cm-1 */

#define A_to_m  (1e-10)
#define A2_to_m2  (1e-20)
#define A3_to_m3  (1e-30)

#define A_to_cm  (1e-8)
#define A2_to_cm2  (1e-16)
#define A3_to_cm3  (1e-24)

#define cm_to_A  (1e8)
#define cm2_to_A2  (1e16)
#define cm3_to_A3  (1e24)

#define erg_to_eV  (6.241460122e11)
#define eV_to_erg  (1.6021892e-12)
/*****
*/

```

```

float *vector(int);
float **matrix(int,int);
float **convert_matrix(float *,int,int,int,int);
double *dvector(int);
double **dmatrix(int,int);
int *ivector(int);
int **imatrix(int,int);
float **submatrix(float **,int,int,int,int,int);
void free_vector(float *);
void free_dvector(double *);
void free_ivector(int *);
void free_matrix(float **, int);
void free_dmatrix(double **, int);
void free_imatrix(int **, int);
void free_submatrix(float **, int);
void free_convert_matrix(float **,int);
void nrerror(char *);

```

```
#define IBM (1)
```

```
/****** Definitions
```

```
*****/
```

```

#define          HEADER          "\nSimulated Annealing /v2 Feb. 4,
1991\n\n"
#define          NATOMS          (15)
#define          XYZ              (0)  /* constraints for movement      */
#define          R_CONST         (1)
#define          TRUE            (1)
#define          FALSE           (0)
#define          NORMAL          (0)  /* atom status possibilities    */
#define          FIXED           (100)
#define          DISSOC          (101)
#define          START           (0)  /* molecule number             */
#define          BEST            (1)
#define          PRES            (2)
#define          TEMP            (3)
#define          FINISH          (4)

#define          AVGNUM          (100)

```

```
/****** Structures
```

```
*****/
```

```
struct configuration {
```

```

int      type,                /* atomic number for present */
          status;             /* 0= normal 101= Dissociated*/
double   m,                   /* mass of atom */
          p[3],                /* momentum. 0 for present */
          r[3],                /* vector from COM to atom */
          d[3],
          dis;
}      mol[5][NATOMS];        /* Arrays of the configs */

struct potential {
    char      name[80];        /* sting corresp to para func */
    void      (*p)();          /* pointer to parameter func */
    double    (*u)(),          /* pointer to potential func */
              (*g)(),          /* pointer to gradient func */
              total[5];        /* total potential */

    double    Dissoc,
              Bcut, Rcut, Re, De,
              Bswitch, Rswitch,
              Conv, Const,
              S0, S1, S2, S3,
              X0, X1, X2,
              Alpha, Beta, Gama, Delta,
              Epsilon, Sigma, Zeta,
              C4, C6, C8, C10, C12,
              L4, L6, L8, L10, L12,
              Var, Rep, N, M;

    double    gtotal[5],
              gC4, gC6, gC8, gC10, gC12,
              gL4, gL6, gL8, gL10, gL12;

} ms, mss, ss;

struct michas {
    double    dE, Vv, Kk, Hh, Uu, Cc;
} average, variance, total, zero = {0.0, 0.0, 0.0, 0.0, 0.0, 0.0};

double radial[1000];

/***** Doubles
*****/

```

double

```

    anneal_num=1.0,
    accept_ratio=0.5,          /* nsucc/nfail          */
    attempts = 1.0,           /* # att to move atoms  */
    BE[5],                    /* the binding energy    */
    com[3],
    dummy[3],
    moves = 1.0,              /* the number of moves made */
    dE=0.0,
    dEcrit,
    dEavg=1.0,
    dEtot=0.0,
    pX,                       /* the step size          */
    pXstart,
    dX,
    d2X,
    pXmin,
    dT,                       /* the change in pT       */
    d2T,                     /* the change in dT       */
    guano,
    pT,                       /* the pseudo temperature */
    pTmin,
    pTstart,
    max_moves,
    max_pos=1.0,
    nattempts=1.0,           /* # most recent attempts */
    nfail=1.0,
    nsucc=1.0,
    r,
    ratio=1.0,
    rn_max=1.0,              /* the random # +- max    */
    stability,
    stability2,
    tmass[5],                /* the total mass         */
    va[3],
    vb[3],
    vab[3];

```

```

/***** Integers
*****/

```

int


```

i,
  j,
  k;

```

```
int
```

```

    start=START,
    temp=TEMP,
    pres=PRES,
    best=BEST,
    finish=FINISH;

```

```
int
```

```

    atoms = 2,
    averaging = 0,
    constraint = XYZ,
    done = FALSE,
    error = FALSE;

```

```
int
```

```

    m_cycle=0,
    ok_avg=0,
    a_cycle=0,
    min_cycle=0;

```

```

/***** Characters & Strings
*****/

```

```
char
```

```

    alchname[80],
    avgname[80],
    dataname1[80],
    dataname2[80],
    dataname3[80],
    dataname4[80],
    error_type[80],
    inname[80],
    outname[80],
    bruname[80],
    disname[80],
    runname[80],
    tempname[80];

```

```

/***** Files
*****/

FILE
    *DATA1,
    *DATA2,
    *DATA3,
    *DATA4,
    *AVGFIL,
    *IN,
    *OUT,
    *RUN;

/*****
*****/

#ifdef SUN
#define MAX_NUM ((MAXLONG)/2)
#define MAX_POS (MAXLONG)
#endif

#ifdef IBM
#define MAX_NUM ((MAXSHORT)/2)
#define MAX_POS (MAXSHORT)
#endif

double Random(double max) { /* return -max to +max */

return(max*((double)random(MAX_POS)-(double)MAX_NUM)/(double)MAX_NUM);
}

double RandomPos(double max) { /* return 0 to max */
return(max*((double)random(MAX_POS))/(double)MAX_POS);
}

/* Vector Utilities */
void ra_error(int n, char *error_text) {
    int i;
    fprintf(stderr, "Now exiting to system due to\n");
    fprintf(stderr, "a %s condition. Type %d.\n", error_text, n);
    exit(1);
}

```

```

void vect_0(double v1[]) {
    v1[0] = v1[1] = v1[2] = 0.0;
}

double vect_mag(double v1[]) {
    return sqrt(v1[0] * v1[0] + v1[1] * v1[1] + v1[2] * v1[2]);
}

double vect_mag2(double v1[]) {
    return (v1[0] * v1[0] + v1[1] * v1[1] + v1[2] * v1[2]);
}

void vect_smult(double prod[], double v1[], double scalar) {
    prod[0] = v1[0] * scalar;
    prod[1] = v1[1] * scalar;
    prod[2] = v1[2] * scalar;
}

void vect_sdiv(double quo[], double v1[], double scalar) {
    quo[0] = v1[0] / scalar;
    quo[1] = v1[1] / scalar;
    quo[2] = v1[2] / scalar;
}

void vect_sub(double diff[], double v1[], double v2[]) {
    diff[0] = v1[0] - v2[0];
    diff[1] = v1[1] - v2[1];
    diff[2] = v1[2] - v2[2];
}

void vect_add(double sum[], double v1[], double v2[]) {
    sum[0] = v1[0] + v2[0];
    sum[1] = v1[1] + v2[1];
    sum[2] = v1[2] + v2[2];
}

double vect_dot(double v1[], double v2[]) {
    return (v1[0] * v2[0] + v1[1] * v2[1] + v1[2] * v2[2]);
}

void vect_cross(double cross[], double v1[], double v2[]) {
    cross[0] = v1[1] * v2[2] - v1[2] * v2[1];
    cross[1] = v1[2] * v2[0] - v1[0] * v2[2];

```

```

    cross[2] = v1[0] * v2[1] - v1[1] * v2[0];
}

void vect_vect(double lv[], double rv[], double **t1) {
    int i, j;
    for (i = 0; i < 3; i++) for (j = 0; j < 3; j++)
        t1[i][j] = lv[i] * rv[j];
}

void vect_copy(double old[], double new[]) {
    new[0] = old[0];
    new[1] = old[1];
    new[2] = old[2];
}

void rotate(double rot[], double v1[], double theta, int z) {
    rot[(z+1)%3] = v1[(z+1)%3] * cos(theta) - v1[(z+2)%3] * sin(theta);
    rot[(z+2)%3] = v1[(z+1)%3] * sin(theta) + v1[(z+2)%3] * cos(theta);
    rot[z] = v1[z];
}

void matrix_smult(double **matout, double **matin, double scaler, int n) {
    double      **temp;
    int          i, j, k;

    temp = dmatrix(n,n);
    for (i = 0; i < n; i++)
        for (j = 0; j < n; j++)
            temp[i][j] = 0.0;
    for (i = 0; i < n; i++)
        for (j = 0; j < n; j++) {
            temp[i][j] = scaler * matin[i][j];
            matout[i][j] = temp[i][j];
        }
}

void matrix_mult(double **matout, double **lmat, double **rmat, int n) {
    int          i, j, k;
    double **temp;
    temp = dmatrix(n,n);
    for (i = 0; i < n; i++)
        for (j = 0; j < n; j++)
            temp[i][j] = 0.0;

```

```

    for (i = 0; i < n; i++)
        for (j = 0; j < n; j++)
            for (k = 0; k < n; k++)
                temp[i][j] += lmat[i][k] * rmat[k][j];

    for (i = 0; i < n; i++)
        for (j = 0; j < n; j++)
            matout[i][j]=temp[i][j];

}

void matrix_trans(double **matout, double **matin,int n) {
    int i, j;
    for (i = 0; i < n; i++)
        for (j = 0; j < n; j++)
            matout[i][j] = matin[j][i];
}

void matrix_vect(double vout[], double **mat, double vin[], int n) {
    double *temp;
    int i, j, k;

    temp=dvector(n);
    for (i = 0; i < n; i++) temp[i] = 0.0;
    for (i = 0; i < n; i++) for (j = 0; j < n; j++)
        temp[i] += vin[j] * mat[i][j];
    for (i = 0; i < n; i++) vout[i] = temp[i];
}

void vect_matrix(double vout[], double vin[], double **mat, int n) {
    double *temp;
    int i, j, k;

    temp=dvector(n);
    for (i = 0; i < n; i++) temp[i] = 0.0;
    for (i = 0; i < n; i++) for (j = 0; j < n; j++)
        temp[i] += vin[j] * mat[j][i];
    for (i = 0; i < n; i++) vout[i] = temp[i];
}

void matrix_print(char name[12],double **mat,int n,int m) {
    int i,j;
    printf("%s\n",name);

```



```

for (i=0;i<n;i++)
{
    printf("|");
    for (j=0;j<m;j++)
        printf(" %9.5g",mat[i][j]);
    printf(" |\n");
}
}

```

```

void vect_print(char name[12],double *vec, int n) {
    int i;
    printf("%s  |",name);
    for (i=0;i<n;i++)
        printf(" %9.5g ",vec[i]);
    printf("|\n\n");
}

```

/***** Numerical Recipes stuff modified for my use *****/

```

void nrerror(char *error_text) {

    fprintf(stderr,"Numerical Recipes run-time error...\n");
    fprintf(stderr,"%s\n",error_text);
    fprintf(stderr,"...now exiting to system...\n");
    exit(1);
}

```

```

float *vector(int n) {
    float *v;

    v=(float *)malloc((unsigned) (n)*sizeof(float));
    if (!v) nrerror("allocation failure in vector()");
    return v;
}

```

```

int *ivector(int n) {
    int *v;

```

```

v=(int *)malloc((unsigned) (n)*sizeof(int));
if (!v) perror("allocation failure in ivector()");
return v;
}

double *dvector(int n) {
    double *v;

    v=(double *)malloc((unsigned) (n)*sizeof(double));
    if (!v) perror("allocation failure in dvector()");
    return v;
}

float **matrix(int nn, int mm) {
    int i;
    float **m;

    m=(float **) malloc((unsigned) (nn)*sizeof(float*));
    if (!m) perror("allocation failure 1 in matrix()");

    for(i=0;i<nn;i++) {
        m[i]=(float *) malloc((unsigned) (mm)*sizeof(float));
        if (!m[i]) perror("allocation failure 2 in matrix()");
    }
    return m;
}

double **dmatrix(int nn, int mm) {
    int i;
    double **m;

    m=(double **) malloc((unsigned) (nn)*sizeof(double*));
    if (!m) perror("allocation failure 1 in dmatrix()");

    for(i=0;i<nn;i++) {
        m[i]=(double *) malloc((unsigned) (mm)*sizeof(double));
        if (!m[i]) perror("allocation failure 2 in dmatrix()");
    }
    return m;
}

int **imatrix(int nn,int mm) {
    int i,**m;

```

```

m=(int **)malloc((unsigned) (nn)*sizeof(int*));
if (!m) perror("allocation failure 1 in imatrix()");

for(i=0;i<nn;i++) {
    m[i]=(int *)malloc((unsigned) (mm)*sizeof(int));
    if (!m[i]) perror("allocation failure 2 in imatrix()");
}
return m;
}

float **submatrix(float **a,int oldrl,int oldrh,int oldcl,int newrl,int newcl)
{
    int i,j;
    float **m;

    m=(float **) malloc((unsigned) (oldrh-oldrl+1)*sizeof(float*));
    if (!m) perror("allocation failure in submatrix()");
    m -= newrl;

    for(i=oldrl,j=newrl;i<=oldrh;i++,j++) m[j]=a[i]+oldcl-newcl;

    return m;
}

void free_vector(float *v) {
    free((char*) (v));
}

void free_ivec(int *v) {
    free((char*) (v));
}

void free_dvec(double *v) {
    free((char*) (v));
}

void free_matrix(float **m, int nn) {
    int i;

```

```

        for(i=nn;i>-1;i--) free((char*) (m[i]));
        free((char*) (m));
    }

void free_dmatrix(double **m,int nn) {
    int i;

    for(i=nn;i>-1;i--) free((char*) (m[i]));
    free((char*) (m));
}

void free_imatrix(int **m,int nn) {
    int i;

    for(i=nn;i>-1;i--) free((char*) (m[i]));
    free((char*) (m));
}

void free_submatrix(float **b,int nrl) {
    free((char*) (b+nrl));
}

float **convert_matrix(float *a,int nrl,int nrh,int ncl,int nch){
    int i,j,nrow,ncol;
    float **m;

    nrow=nrh-nrl+1;
    ncol=nch-ncl+1;
    m = (float **) malloc((unsigned) (nrow)*sizeof(float*));
    if (!m) perror("allocation failure in convert_matrix()");
    m -= nrl;
    for(i=0,j=nrl;i<=nrow-1;i++,j++) m[j]=a+ncol*i-ncl;
    return m;
}

void free_convert_matrix(float **b,int nrl) {
    free((char*) (b+nrl));
}

void jacobi(double **mat,int n,double *d, double **v,int *nrot) {
#define ROTATE(a,i,j,k,l) g=a[i][j];h=a[k][l];a[i][j]=g-s*(h+g*tau);\
    a[k][l]=h+s*(g-h*tau);

```

```

int j,iq,ip,i;
double tresh,theta,tau,t,sm,s,h,g,c,*b,*z,*dvector();
void nrerror(),free_dvector();
b=dvector(n);
z=dvector(n);
for (ip=0;ip<n;ip++) {
    for (iq=0;iq<n;iq++) v[ip][iq]=0.0;
    v[ip][ip]=1.0;
}
for (ip=0;ip<n;ip++) {
    b[ip]=d[ip]=mat[ip][ip];
    z[ip]=0.0;
}
*nrot=0;
for (i=0;i<50;i++) {
    sm=0.0;
    for (ip=0;ip<n-1;ip++) {
        for (iq=ip+1;iq<n;iq++)
            sm += fabs(mat[ip][iq]);
    }
    if (sm == 0.0) {
        free_dvector(z);
        free_dvector(b);
        return;
    }
    if (i < 3)
        tresh=0.2*sm/(n*n);
    else
        tresh=0.0;
    for (ip=0;ip<n-1;ip++) {
        for (iq=ip+1;iq<n;iq++) {
            g=100.0*fabs(mat[ip][iq]);
            if (i > 3 && fabs(d[ip])+g == fabs(d[ip])
                && fabs(d[iq])+g == fabs(d[iq]))
                mat[ip][iq]=0.0;
            else if (fabs(mat[ip][iq]) > tresh) {
                h=d[iq]-d[ip];
                if (fabs(h)+g == fabs(h))
                    t=(mat[ip][iq])/h;
                else {
                    theta=0.5*h/(mat[ip][iq]);
                    t=1.0/(fabs(theta)+sqrt(1.0+theta*theta));
                }
            }
        }
    }
}

```



```

        if (theta < 0.0) t = -t;
    }
    c=1.0/sqrt(1+t*t);
    s=t*c;
    tau=s/(1.0+c);
    h=t*mat[ip][iq];
    z[ip] -= h;
    z[iq] += h;
    d[ip] -= h;
    d[iq] += h;
    mat[ip][iq]=0.0;
    for (j=0;j<ip-1;j++) {
        ROTATE(mat,j,ip,j,iq)
    }
    for (j=ip+1;j<iq-1;j++) {
        ROTATE(mat,ip,j,j,iq)
    }
    for (j=iq+1;j<n;j++) {
        ROTATE(mat,ip,j,iq,j)
    }
    for (j=0;j<n;j++) {
        ROTATE(v,j,ip,j,iq)
    }
    ++(*nrot);
}

}

}
for (ip=0;ip<n;ip++) {
    b[ip] += z[ip];
    d[ip]=b[ip];
    z[ip]=0.0;
}

}

nerror("Too many iterations in routine JACOBI");
#undef ROTATE
}

```

```

/***** Elemental Masses (in amu)
*****/
struct elements {
    double m,a;          /* mass and polarizability */
    char *n;             /* atomic symbol */
}

```

```
}    A[110];
```

```
void atomic_mass()
```

```
{
  A[1].m=(1.00794);A[2].m=(4.002602);A[3].m=(6.941);A[4].m=(9.012182);
  A[5].m=(10.811);A[6].m=(12.011);A[7].m=(14.00674);A[8].m=(15.9994);
  A[9].m=(18.9984032);A[10].m=(20.1797);A[11].m=(22.989768);A[12].m=(24.3050);
  A[13].m=(26.981539);A[14].m=(28.0855);A[15].m=(30.973762);A[16].m=(32.066);
  A[17].m=(35.4527);A[18].m=(39.948);A[19].m=(39.0983);A[20].m=(40.078);
  A[21].m=(44.955910);A[22].m=(47.88); A[23].m=(50.9415);A[24].m=(51.9961);
  A[25].m=(54.93805);A[26].m=(55.847);A[27].m=(58.93320);A[28].m=(58.69);
  A[29].m=(63.546);A[30].m=(65.39);A[31].m=(69.723);A[32].m=(72.61);
  A[33].m=(74.92159);A[34].m=(78.96);A[35].m=(79.904);A[36].m=(83.80);
  A[37].m=(85.4678);A[38].m=(87.62);A[39].m=(88.90585);A[40].m=(91.224);
  A[41].m=(92.90638);A[42].m=(95.94);A[43].m=(98.9063);A[44].m=(101.07);
  A[45].m=(102.90550);A[46].m=(106.42);A[47].m=(107.8682);A[48].m=(112.411);
  A[49].m=(114.82);A[50].m=(118.710);A[51].m=(121.75);A[52].m=(127.60);
  A[53].m=(126.90447);A[54].m=(131.29);A[55].m=(132.90543);A[56].m=(137.327);
  A[57].m=(138.9055);A[58].m=(140.115);A[59].m=(140.90765);A[60].m=(144.24);
  A[61].m=(146.9151);A[62].m=(150.36);A[63].m=(151.965);A[64].m=(157.25);
  A[65].m=(158.92534);A[66].m=(162.50);A[67].m=(164.93032);A[68].m=(167.26);
  A[69].m=(168.93421);A[70].m=(173.04);A[71].m=(174.967);A[72].m=(174.49);
  A[73].m=(180.9479);A[74].m=(183.85);A[75].m=(186.207);A[76].m=(190.2);
  A[77].m=(192.22);A[78].m=(195.08);A[79].m=(196.96654);A[80].m=(200.59);
  A[81].m=(204.3833);A[82].m=(207.2);A[83].m=(208.98037);A[84].m=(208.9824);
  A[85].m=(209.9871);A[86].m=(222.0176);A[87].m=(223.0197);A[88].m=(226.0254);
  A[89].m=(227.0278);A[90].m=(232.0381);A[91].m=(231.0359);A[92].m=(238.0289);
  A[93].m=(237.0482);A[94].m=(244.0642);A[95].m=(243.0614);A[96].m=(247.0703);
  A[97].m=(247.0703);A[98].m=(251.0796);A[99].m=(252.0829);A[100].m=(257.0951);
}
```

```
/****** Elemental Symbols
```

```
*****/
```

```
void atomic_symbol()
```

```
{
  A[1].n="H";A[2].n="He";A[3].n="Li";A[4].n="Be";A[5].n="B";A[6].n="C";
  A[7].n="N";A[8].n="O";A[9].n="F";A[10].n="Ne";A[11].n="Na";A[12].n="Mg";
  A[13].n="Al";A[14].n="Si";A[15].n="P";A[16].n="S";A[17].n="Cl";A[18].n="Ar";
  A[19].n="K";A[20].n="Ca";A[21].n="Sc";A[22].n="Ti";A[23].n="V";A[24].n="Cr";
  A[25].n="Mn";A[26].n="Fe";A[27].n="Co";A[28].n="Ni";A[29].n="Cu";A[30].n="Zn";
```

```

A[31].n="Ga";A[32].n="Ge";A[33].n="As";A[34].n="Se";A[35].n="Br";A[36].n="Kr";
A[37].n="Rb";A[38].n="Sr";A[39].n="Y";A[40].n="Zr";A[41].n="Nb";A[42].n="Mo";
A[43].n="Tc";A[44].n="Ru";A[45].n="Rh";A[46].n="Pd";A[47].n="Ag";A[48].n="Cd";
A[49].n="In";A[50].n="Sn";A[51].n="Sb";A[52].n="Te";A[53].n="I";A[54].n="Xe";
A[55].n="Cs";A[56].n="Ba";A[57].n="La";A[58].n="Ce";A[59].n="Pr";A[60].n="Nd";
A[61].n="Pm";A[62].n="Sm";A[63].n="Eu";A[64].n="Gd";A[65].n="Tb";A[66].n="Dy";
A[67].n="Ho";A[68].n="Er";A[69].n="Tm";A[70].n="Yb";A[71].n="Lu";A[72].n="Hf";
A[73].n="Ta";A[74].n="W";A[75].n="Re";A[76].n="Os";A[77].n="Ir";A[78].n="Pt";
A[79].n="Au";A[80].n="Hg";A[81].n="Tl";A[82].n="Pb";A[83].n="Bi";A[84].n="Po";
A[85].n="At";A[86].n="Rn";A[87].n="Fr";A[88].n="Ra";A[89].n="Ac";A[90].n="Th";
A[91].n="Pa";A[92].n="U";A[93].n="Np";A[94].n="Pu";A[95].n="Am";A[96].n="Cm";
A[97].n="Bk";A[98].n="Cf";A[99].n="Es";A[100].n="Fm";
}

```

```

/***** atomic polarizability

```

```

*****/

```

```

void atomic_alpha()

```

```

{
  A[2].a = 0.206;
  A[10].a = 0.397;
  A[18].a = 1.67;
  A[36].a = 2.52;
  A[54].a = 4.11;
}

```

```

/*

```

```

* The potential functions which will be pointed to by double pointers.

```

```

*/

```

```

double

```

```

    r1, r2, r3, r4, r5, r6, r7, r8, r9, r10, r11, r12, r13, r14, r15;

```

```

/* The zero potential */

```

```

double u0(double r) {
    return(r*0.0);
}

```

```

/* EIGHT FOUR POTENTIAL */

```

```

double u84(double r) {
    r4 = r * r;
    r4 *= r4;
    r8 = r4 * r4;

```

```

    return ((ms.C8/r8) - (ms.C4/r4));
}

```

```

/* LJ 12-6 */
double uLJ126(double r) {
    double ret;

    r6=r*r*r;
    r6*=r6;
    r12=r6*r6;
    return((ss.L12/r12)-(ss.L6/r6));
}

```

```

/* MSV III Ar-Ar POTENTIAL */
double uMSVIII(double r1) {
    double      ret, r, t;

    r= r1/ss.Re;

    if (r<=ss.X1) {
        ret = exp(-2.0* ss.Beta * (r - 1));
        ret -= 2.0 * exp(-ss.Beta * (r - 1));
    } else if (r<=ss.X2) {
        t = r - ss.X1;
        ret = ss.S0+t*(ss.S1+(r-ss.X2)*(ss.S2+t*ss.S3));
    } else {
        r8 = r*r;
        r6 = r8*r8*r8;
        r8 *= r6;
        ret = (ss.C6 / r6) + (ss.C8 / r8);
    }
    ret *= ss.De;
    return(ret);
}

```

```

/* MORSE SWITCH 4 */
double uMSw4(double r) {
    double      morse, fsw=1.0,v4;

    fsw /= (1.0 + exp(-ms.Bswitch*( r - ms.Rswitch)));
}

```

```

morse = -ms.Beta * (r - ms.Re);
morse = 1.0 - exp(morse);
morse *= morse;
morse -= 1.0;
morse *= ms.De;
if (r>0.05) {
    r4 = r*r;
    r4 *= r4;
    v4 = (-ms.C4/r4);
} else v4 = (-ms.C4/6.25e-6);
return((fsw * v4) + ((1.0-fsw) * morse));
}

```

```

/* ASHER Ar-Ar POTENTIAL */
double uASHER(double r1) {
    double      ret, r, t;

    r= r1/ss.Re;

    if (r1<=ss.X0) {
        r6=r1*r1*r1;
        r6*=r6;
        r12=r6*r6;
        return((ss.L12/r12)-(ss.L6/r6));
    } else if (r<=ss.X1) {
        ret = exp(-2.0* ss.Beta * (r - 1));
        ret -= 2.0 * exp(-ss.Beta * (r - 1));
    } else if (r<=ss.X2) {
        t = r - ss.X1;
        ret = ss.S0+t*(ss.S1+(r-ss.X2)*(ss.S2+t*ss.S3));
    } else {
        r8 = r*r;
        r6 = r8*r8*r8;
        r8 *= r6;
        ret = (ss.C6 / r6) + (ss.C8 / r8);
    }
    ret *= ss.De;
    return(ret);
}

```

```

/* n(rbar)-6 Potential */

```



```

double uN6(double r1) {
    double      ret, r, rN, Aaa, Bbb, tempn;

    r = r1/ss.Re;
    r6 = r * r * r;
    r6 *= r6;
    ss.N = (ss.Gama * (r-1.0)) + ss.M;
    rN = pow(r,ss.N);
    tempn = ss.N - 6.0;
    Aaa = 6.0/tempn;
    Bbb = ss.N/tempn;
    ret = Aaa/rN;
    ret -= Bbb/r6;
    ret *= ss.De;
    return(ret);
}

```

/* CHARGE INDUCED DIPOLE - CHARGE INDUCED DIPOLE */

```

double uINDPDP(double cca[],double ccb[], double cc0[]) {
    double      ret, va[3], vb[3], vab[3],
               r, ra, rb;

    vect_sub(va,cca,cc0);
    vect_sub(vb,ccb,cc0);
    vect_sub(vab,va,vb);
    r = vect_mag(vab);
    r2= r*r;
    ra = vect_mag(va);
    rb = vect_mag(vb);
    r3 = (r*ra*rb);
    r3 *= r3*r3;
    ret = (-3.0 * vect_dot(va,vab) * vect_dot(vb,vab));
    ret /= r2;
    ret += vect_dot(va,vb);
    ret *= (mss.Const/r3);
    return(ret);
}

```

```
/* MORSE POTENTIAL */
```

```
double uMORSE(double r) {
    double ret;

    ret = -ss.Beta * (r - ss.Re);
    ret = 1-exp(ret);
    ret *= ret;
    ret -= 1.0;
    ret *= ss.De;
    return(ret);
}
```

```
/* CHARGE INDUCED DIPOLE - CHARGE INDUCED DIPOLE */
```

```
double uINDPDP_WC(double cca[], double ccb[], double cc0[]) {
    double ret, va[3], vb[3], vab[3],
           r, ra, rb;

    vect_sub(va,cca,cc0);
    vect_sub(vb,ccb,cc0);
    vect_sub(vab,va,vb);
    r = vect_mag(vab);
    r2= r*r;
    ra = vect_mag(va);
    rb = vect_mag(vb);
    r3 = (r*ra*rb);
    r3 *= r3*r3;
    ret = (-3.0 * vect_dot(va,vab) * vect_dot(vb,vab));
    ret /= r2;
    ret += vect_dot(va,vb);
    ret *= mss.Const/r3;

    ret /= (1+exp(-mss.Bcut*(r-mss.Rcut)));

    return(ret);
}
```

```
/*
```

```
* The gradients for the above functions which have been determined for most
* of the simple potentials.
```

```
*/
```

```
double g0(double r) {
    return(r*0.0);
}
```

```
/* EIGHT FOUR GRADIENT */
```

```
double g84(double r) {
    r4 = r * r;
    r4 *= r4;
    r5 = r4 * r;
    r9 = r4 * r4 * r;
    return ((ms.gC4/r5) - (ms.gC8/r9));
}
```

```
/* LJ 12-6 GRADIENT */
```

```
double gLJ126(double r) {
    double ret;

    r6 = r * r * r;
    r6 *= r6;
    r7 = r6 * r;
    r13 = r6 * r6 * r;
    return((ss.gL6/r7)-(ss.gL12/r13));
}
```

```
/* MORSE POTENTIAL GRADIENT */
```

```
double gMORSE(double r) {
    double ret,a;

    a = -ss.Beta * (r - ss.Re);
    ret = exp(a) - exp(2.0*a);
    ret *= ss.De * 2.0 * ss.Beta;
    return(ret);
}
```

```
/*
```

```
* The parameter functions which initialize appropriate variables and
* assign the pointer ms.u or ss.u etc to the correct potential function.
```

```
*/
```

```

void pms0() {
    ms.u=u0;
    ms.g=g0;
    strcpy(ms.name,"pms0\0");
    /*      printf("\nZero ms potential.\n");      */
}

```

```

void pmss0() {
    mss.u=u0;
    mss.g=g0;
    strcpy(mss.name,"pmss0\0");
    /*      printf("\nZero mss potential.\n");      */
}

```

```

void pss0() {
    ss.u=u0;
    ss.g=g0;
    strcpy(ss.name,"pss0\0");
    /*      printf("\nZero ss potential.\n");      */
}

```

/****** Gas - Gas parameters

******/

```

void pMSVIII() {
    ss.u=uMSVIII;

    ss.Beta      =      6.279;          /* Morse Spline van der Waals      */
    ss.S0  =      -0.7;          /* Lee et. al. Ar-Ar parameters      */
    ss.S1  =      1.8337;
    ss.S2  =      -4.5740;
    ss.S3  =      4.3667;
    ss.C6  =      -1.180;
    ss.C8  =      -0.6118;
    ss.De  =      0.01207;
    ss.Re  =      3.76;
    ss.X1  =      1.12636;
    ss.X2  =      1.400;
}

```

```

void
pASHER() {
    ss.u=uASHER;

```

```

/* Asher & Lee et. al. Ar - Ar */
ss.Beta = 6.279; /* Morse Spline van der Waals */
ss.S0 = -0.7; /* Lee et. al. Ar-Ar parameters */
ss.S1 = 1.8337;
ss.S2 = -4.5740;
ss.S3 = 4.3667;
ss.C6 = -1.180;
ss.C8 = -0.6118;
ss.De = 0.01207;
ss.Re = 3.76;
ss.Sigma = ss.Re-(log(2.0))/ss.Beta;
ss.X0 = ss.Sigma;
ss.X1 = 1.12636;
ss.X2 = 1.400;
ss.Epsilon = ss.De*ss.Beta*ss.Sigma/6.0;
ss.L6 = ss.Sigma*ss.Sigma;
ss.L6 *= ss.L6*ss.L6;
ss.L12 = ss.Epsilon*ss.L6*ss.L12*ss.L12;
ss.L6 *= ss.Epsilon;
}

void pLJ126ArAr() {
    ss.u=uLJ126;

    ss.Re=3.76;
    ss.De=0.01207;
    ss.Sigma = ss.Re*pow(0.5,(1.0/6.0));
    ss.L6 = ss.Sigma * ss.Sigma * ss.Sigma;
    ss.L6 *= ss.L6;
    ss.L12 = 4.0 * ss.L6 * ss.L6 * ss.De;
    ss.L6 *= 4.0 * ss.De;
}

void pLJ126KrKr() {
    ss.u=uLJ126;

    ss.Sigma = 3.83;
    ss.Epsilon = 0.014132448;
    ss.L6 = ss.Sigma*ss.Sigma;
    ss.L6 *= ss.L6*ss.L6;
    ss.L12 = 4.0*ss.Epsilon*ss.L6*ss.L6;
    ss.L6 *= 4.0*ss.Epsilon;
}

```



```
void pN6ArAr() {  
    ss.u=uN6;  
  
    ss.M = 13.0;  
    ss.Gama = 9.0;  
    ss.Re = 3.902;  
    ss.De = 0.012197854;  
}
```

```
void pN6KrKr() {  
    ss.u=uN6;  
  
    ss.M = 13.0;  
    ss.Gama = 10.0;  
    ss.Re = 4.02;  
    ss.De = 0.0171165754;  
}
```

```
void pN6XeXe() {  
    ss.u=uN6;  
  
    ss.M = 13.0;  
    ss.Gama = 10.0;  
    ss.Re = 4.36;  
    ss.De = 0.024214744;  
}
```

```
void pN6ArKr() {  
    ss.u=uN6;  
  
    ss.M = 13.0;  
    ss.Gama = 9.0;  
    ss.Re = 3.902;  
    ss.De = 0.014218622;  
}
```

```
void pN6ArXe() {  
    ss.u=uN6;  
  
    ss.M = 13.0;  
    ss.Gama = 10.0;  
    ss.Re = 4.06;  
    ss.De = 0.016148907;
```

```

}

/***** Metal - Gas parameters
*****/
void pLJ126ArArPJB() {
    ss.u=uLJ126;

    ss.Sigma = 3.405;
    ss.Epsilon = 120.0;
    ss.L6 = ss.Sigma*ss.Sigma;
    ss.L6 *= ss.L6*ss.L6;
    ss.Conv =KBOLTZ/(CSPEED * HPLANK * EV2CM);
    ss.L12 = 4.0*ss.Epsilon*ss.L6*ss.L6*ss.Conv;
    ss.L6 *= 4.0*ss.Epsilon*ss.Conv;
}

void p84() {
    ms.C8= (ms.C4 * ms.C4)/(4.0 * ms.De);
    ms.C4*= erg_to_eV * 1e8;
    ms.C8*= erg_to_eV * erg_to_eV *1e16;
}

void p84De() {
    ms.u=u84;

    ms.De= mss.Var;
    ms.C4= A[18].a * QeSTAT2 /2.0;
    p84();
}

void p84CoAr() {
    ms.u=u84;

    ms.De= 0.524;
    ms.C4= A[18].a * QeSTAT2 /2.0;
    p84();
}

void p84VAr() {
    ms.u=u84;

    ms.De= 0.381;

```

```

    ms.C4= A[18].a * QeSTAT2 / 2.0;
    p84();
}

```

```

void p84CoKr() {
    ms.u=u84;

    ms.De= 0.682;
    ms.C4= A[36].a * QeSTAT2 /2.0;
    p84();
}

```

```

void p84VKr() {
    ms.u=u84;

    ms.De= 0.485;
    ms.C4= A[36].a * QeSTAT2 / 2.0;
    p84();
}

```

```

void pMSw4CoArCB() {
    ms.u=uMSw4;

    ms.C4 = A[18].a * QeSTAT2 /2.0;
    ms.C4 *= erg_to_eV * 1e8;
    ms.De = 0.403271;
    ms.Re = 2.433;
    ms.Beta = 1.839536;
    ms.Rswitch = 3.9093361;
    ms.Bswitch = 2.0*ms.Beta;
}

```

```

void pMSw4VArCB() {
    ms.u=uMSw4;

    ms.C4 = A[18].a * QeSTAT2 /2.0;
    ms.C4 *= erg_to_eV * 1e8;
    ms.De = 0.299168;
    ms.Re = 2.6438;
    ms.Beta = 1.679003;
    ms.Rswitch = 4.3640867;
    ms.Bswitch = 2.0*ms.Beta;
}

```

```

void pMSw4CoArPJB() {
    ms.u=uMSw4;

    ms.C4= A[18].a * QeSTAT2 /2.0;
    ms.C4*= erg_to_eV * 1e8;
    ms.De=0.510371;
    ms.Re=1.84;
    ms.Beta=1.977797;
    ms.Rswitch=1.5*ms.Re;
    ms.Bswitch=2.0*ms.Beta;
}

```

```

void pMSw4VArPJB() {
    ms.u=uMSw4;

    ms.C4= A[18].a * QeSTAT2 /2.0;
    ms.C4*= erg_to_eV * 1e8;
    ms.De=0.370816;
    ms.Re=1.99;
    ms.Beta=1.820232;
    ms.Rswitch=1.5*ms.Re;
    ms.Bswitch=2.0*ms.Beta;
}

```

```

void pMSw4CoArRLA() {
    ms.u=uMSw4;

    ms.C4= A[18].a * QeSTAT2 /2.0;
    ms.C4*= erg_to_eV * 1e8;
    ms.De=0.481518;
    ms.Re=1.84;
    ms.Beta=2.5;
    ms.Rswitch=2.34045;
    ms.Bswitch=5.0;
}

```

```

void pMSw4VArRLA() {
    ms.u=uMSw4;

    ms.C4= A[18].a * QeSTAT2 /2.0;
    ms.C4*= erg_to_eV * 1e8;
    ms.De=0.367235;
    ms.Re=1.99;
}

```

```

    ms.Beta=2.05;
    ms.Rswitch=2.8;
    ms.Bswitch=4.1;
}

void pMSw4CoArET() {
    ms.u=uMSw4;

    ms.C4= A[18].a * QeSTAT2 /2.0;
    ms.C4*= erg_to_eV * 1e8;
    ms.De=0.403271;
    ms.Re=2.433;
    ms.Beta=1.839536;
    ms.Rswitch=3.9093361;
    ms.Bswitch=2*ms.Beta;
}

void pMSw4VArET() {
    ms.u=uMSw4;

    ms.C4= A[18].a * QeSTAT2 /2.0;
    ms.C4*= erg_to_eV * 1e8;
    ms.De=0.299168;
    ms.Re=2.6438;
    ms.Beta=1.679003;
    ms.Rswitch=4.3640867;
    ms.Bswitch=2.0*ms.Beta;
}

void pMS4_MAr() {
    ms.u=uMSw4;

    ms.C4= A[18].a * QeSTAT2 /2.0;
    ms.C4*= erg_to_eV * 1e8;
    ms.De=0.299168;
    ms.Re=2.6438;
    ms.Beta=1.679003;
    ms.Rswitch=4.3640867;
    ms.Bswitch=2.0*ms.Beta;
}

void pINDPDP() {
    mss.u=uINDPDP;

```



```

    mss.Alpha=A[18].a;
    mss.Beta=A[18].a;
    mss.Conv=6.241460122e19;
    mss.Const=(mss.Conv * QeSTAT2 * mss.Alpha * mss.Beta);
}

void pINDPDP_WC_ORIG() {
    mss.u=uINDPDP_WC;

    mss.Alpha=A[18].a;
    mss.Beta=A[18].a;
    mss.Bcut=1.6699468;
    mss.Rcut=5.264;
    mss.Conv=6.241460122e19;
    mss.Const=(mss.Conv * QeSTAT2 * mss.Alpha * mss.Beta);
}

void pINDPDP_WC_MIN() {
    mss.u=uINDPDP_WC;

    mss.Alpha=A[18].a;
    mss.Beta=A[18].a;
    mss.Bcut=10.0;
    mss.Rcut=2.0;
    mss.Conv=6.241460122e19;
    mss.Const=(mss.Conv * QeSTAT2 * mss.Alpha * mss.Beta);
}

void pINDPDP_WC_VARY() {
    mss.u=uINDPDP_WC;

    mss.Alpha=A[18].a;
    mss.Beta=A[18].a;
    mss.Bcut=10.0;
    mss.Rcut=mss.Var;
    mss.Conv=6.241460122e19;
    mss.Const=(mss.Conv * QeSTAT2 * mss.Alpha * mss.Beta);
}

/* assign_potentials() assigns the parameters for the potential and the pointer
 * to the potential. In this way values for parameters may be varied by use of
 * special functions which calculate new parameters based upon new De, Re...
 */

```

```

void assign_potentials() {
    struct potential *P[3];
    int i;

    P[0]= &ms;
    P[1]= &ss;
    P[2]= &mss;

    for(i=0;i<3;i++) {
        (*P[i]).Bcut=      0.0;
        (*P[i]).Rcut=      0.0;
        (*P[i]).Re=        0.0;
        (*P[i]).De=        0.0;
        (*P[i]).Bswitch=   0.0;
        (*P[i]).Rswitch=   0.0;
        (*P[i]).Conv=      0.0;
        (*P[i]).Const=     0.0;
        (*P[i]).S0=        0.0;
        (*P[i]).S1=        0.0;
        (*P[i]).S2=        0.0;
        (*P[i]).S3=        0.0;
        (*P[i]).X0=        0.0;
        (*P[i]).X1=        0.0;
        (*P[i]).X2=        0.0;
        (*P[i]).Alpha=     0.0;
        (*P[i]).Beta=      0.0;
        (*P[i]).Gama=      0.0;
        (*P[i]).Delta=     0.0;
        (*P[i]).Epsilon=   0.0;
        (*P[i]).Sigma=     0.0;
        (*P[i]).Zeta=      0.0;
        (*P[i]).C4=        0.0;
        (*P[i]).C6=        0.0;
        (*P[i]).C8=        0.0;
        (*P[i]).C10=       0.0;
        (*P[i]).C12=       0.0;
        (*P[i]).L4=        0.0;
        (*P[i]).L6=        0.0;
        (*P[i]).L8=        0.0;
        (*P[i]).L10=       0.0;
        (*P[i]).L12=       0.0;
        (*P[i]).Rep=       0.0;
        (*P[i]).N=         0.0;
    }
}

```

```

        (*P[i]).M=          0.0;
    }

    if      (!strcmp(ms.name,"p84CoAr"))      ms.p=p84CoAr;
    else if (!strcmp(ms.name,"p84De"))        ms.p=p84De;
    else if (!strcmp(ms.name,"p84VAr"))        ms.p=p84VAr;
    else if (!strcmp(ms.name,"p84CoKr"))       ms.p=p84CoKr;
    else if (!strcmp(ms.name,"p84VKr"))        ms.p=p84VKr;
    else if (!strcmp(ms.name,"pMSw4CoArCB"))    ms.p=pMSw4CoArCB;
    else if (!strcmp(ms.name,"pMSw4VArCB"))    ms.p=pMSw4VArCB;
    else if (!strcmp(ms.name,"pMSw4CoArPJB"))   ms.p=pMSw4CoArPJB;
    else if (!strcmp(ms.name,"pMSw4VArPJB"))   ms.p=pMSw4VArPJB;
    else if (!strcmp(ms.name,"pMSw4CoArRLA"))   ms.p=pMSw4CoArRLA;
    else if (!strcmp(ms.name,"pMSw4VArRLA"))   ms.p=pMSw4VArRLA;
    else if (!strcmp(ms.name,"pMSw4CoArET"))   ms.p=pMSw4CoArET;
    else if (!strcmp(ms.name,"pMSw4VArET"))   ms.p=pMSw4VArET;
    else                                       ms.p=pms0;

    if      (!strcmp(ss.name,"pMSVIII"))        ss.p=pMSVIII;
    else if (!strcmp(ss.name,"pASHER"))         ss.p=pASHER;
    else if (!strcmp(ss.name,"pLJ126ArAr"))     ss.p=pLJ126ArAr;
    else if (!strcmp(ss.name,"pLJ126KrKr"))     ss.p=pLJ126KrKr;
    else if (!strcmp(ss.name,"pLJ126ArArPJB"))  ss.p=pLJ126ArArPJB;
    else if (!strcmp(ss.name,"pN6ArAr"))        ss.p=pN6ArAr;
    else if (!strcmp(ss.name,"pN6ArKr"))        ss.p=pN6ArKr;
    else if (!strcmp(ss.name,"pN6ArXe"))        ss.p=pN6ArXe;
    else if (!strcmp(ss.name,"pN6KrKr"))        ss.p=pN6KrKr;
    else ss.p=pss0;

    if      (!strcmp(mss.name,"pINDPDP"))       mss.p=pINDPDP;
    else if (!strcmp(mss.name,"pINDPDP_WC_ORIG"))
mss.p=pINDPDP_WC_ORIG;
        else if (!strcmp(mss.name,"pINDPDP_WC_MIN"))
mss.p=pINDPDP_WC_MIN;
        else if (!strcmp(mss.name,"pINDPDP_WC_VARY"))
mss.p=pINDPDP_WC_VARY;
    else                                       mss.p=pmss0;

    ms.Dissoc = 15.0;

    for(i=0;i<3;i++) {
        (void)(*P[i]).p();
        printf("%s Potential\n",(*P[i]).name);
    }

```

```

if( (*P[i]).Bcut != 0.0)
    printf("Bcut= %g\n",(*P[i]).Bcut);
if( (*P[i]).Rcut != 0.0)
    printf("Rcut= %g\n",(*P[i]).Rcut);
if( (*P[i]).De != 0.0)
    printf("De= %g\n",(*P[i]).De);
if( (*P[i]).Re != 0.0)
    printf("Re= %g\n",(*P[i]).Re);
if( (*P[i]).Bswitch != 0.0)
    printf("Bswitch= %g\n",(*P[i]).Bswitch);
if( (*P[i]).Rswitch != 0.0)
    printf("Rswitch= %g\n",(*P[i]).Rswitch);
if( (*P[i]).Conv != 0.0)
    printf("Conv= %g\n",(*P[i]).Conv);
if( (*P[i]).S0 != 0.0)
    printf("S0= %g\n",(*P[i]).S0);
if( (*P[i]).S1 != 0.0)
    printf("S1= %g\n",(*P[i]).S1);
if( (*P[i]).S2 != 0.0)
    printf("S2= %g\n",(*P[i]).S2);
if( (*P[i]).S3 != 0.0)
    printf("S3= %g\n",(*P[i]).S3);
if( (*P[i]).X0 != 0.0)
    printf("X0= %g\n",(*P[i]).X0);
if( (*P[i]).X1 != 0.0)
    printf("X1= %g\n",(*P[i]).X1);
if( (*P[i]).X2 != 0.0)
    printf("X2= %g\n",(*P[i]).X2);
if( (*P[i]).C4 != 0.0)
    printf("C4= %g\n",(*P[i]).C4);
if( (*P[i]).C6 != 0.0)
    printf("C6= %g\n",(*P[i]).C6);
if( (*P[i]).C8 != 0.0)
    printf("C8= %g\n",(*P[i]).C8);
if( (*P[i]).C10 != 0.0)
    printf("C10= %g\n",(*P[i]).C10);
if( (*P[i]).C12 != 0.0)
    printf("C12= %g\n",(*P[i]).C12);
if( (*P[i]).L4 != 0.0)
    printf("L4= %g\n",(*P[i]).L4);
if( (*P[i]).L6 != 0.0)
    printf("L6= %g\n",(*P[i]).L6);
if( (*P[i]).L8 != 0.0)

```

```

        printf("L8= %g\n",(*P[i]).L8);
    if( (*P[i]).L10 != 0.0)
        printf("L10= %g\n",(*P[i]).L10);
    if( (*P[i]).L12 != 0.0)
        printf("L12= %g\n",(*P[i]).L12);
    if( (*P[i]).Alpha != 0.0)
        printf("Alpha= %g\n",(*P[i]).Alpha);
    if( (*P[i]).Beta != 0.0)
        printf("Beta= %g\n",(*P[i]).Beta);
    if( (*P[i]).Gama != 0.0)
        printf("Gama= %g\n",(*P[i]).Gama);
    if( (*P[i]).Delta != 0.0)
        printf("Delta= %g\n",(*P[i]).Delta);
    if( (*P[i]).Epsilon != 0.0)
        printf("Epsilon= %g\n",(*P[i]).Epsilon);
    if( (*P[i]).Sigma != 0.0)
        printf("Sigma= %g\n",(*P[i]).Sigma);
    if( (*P[i]).Zeta != 0.0)
        printf("Zeta= %g\n",(*P[i]).Zeta);
    if( (*P[i]).Var != 0.0)
        printf("Var= %g\n",(*P[i]).Var);
    if( (*P[i]).Rep != 0.0)
        printf("Rep= %g\n",(*P[i]).Rep);
    if( (*P[i]).M != 0.0)
        printf("M= %g\n",(*P[i]).M);
    if( (*P[i]).N != 0.0)
        printf("N= %g\n",(*P[i]).N);
    printf("\n\n");
}
}

/* Calculate the potential associated with the pointers u.ms, u.ss & u.mss. */

double calc_potential(int num) {
    int i,j;
    ms.total[num]=0.0;
    ss.total[num]=0.0;
    mss.total[num]=0.0;
    if(ms.p != pms0) {
        for(i=1;i<atoms;i++) {
            vect_sub(va,mol[num][i].r,mol[num][0].r);
            r=vect_mag(va);

```



```

        /* check if any atoms are dissociated */
        mol[num][i].status = (r>ms.Dissoc)
            ? DISSOC : mol[num][i].status;
        ms.total[num] += (double)ms.u(r);
    }
}
if(ss.p != pss0) {
    for(i=1;i<atoms;i++) for(j=i+1;j<atoms;j++) {
        vect_sub(vab,mol[num][i].r,mol[num][j].r);
        r=vect_mag(vab);
        ss.total[num] += (double)ss.u(r);
    }
}
if(mss.p != pmss0) {
    for(i=1;i<atoms;i++) for(j=i+1;j<atoms;j++)
        mss.total[num] +=
            (double)mss.u((mol[num][i].r),(mol[num][j].r),(mol[num][0].r));
}
return(ms.total[num] + ss.total[num] + mss.total[num]);
}

/* read_config opens the config file and reads in the parameters. Function
 * returns a 2 if unsuccessful 0 otherwise.
 */
int
read_config(char *filename) {
    if ((IN = fopen(filename, "r")) == NULL) {
        printf("\nCan't open the file [%s].\n",filename);
        return(2);
    }
    fscanf(IN, "%d %lf %lf",
           &atoms,
           &max_moves,
           &dEcrit);
    fscanf(IN, "%lf %lf %lf %lf",
           &pTstart,
           &pTmin,
           &dT,
           &d2T);
    fscanf(IN, "%lf %lf %lf %lf",
           &pXstart,
           &pXmin,
           &dX,

```

```

        &d2X);
fscanf(IN, "%lf %lf %lf %lf",
        &(ms.total[start]),
        &(ss.total[start]),
        &(mss.total[start]),
        &BE[start]);
fscanf(IN, "%s %s %s %lf",
        ms.name,
        ss.name,
        mss.name,
        &(mss.Var));
for (i = 0; i < atoms; i++)
    fscanf(IN, "%d %lf %lf %lf %lf %d %lf",
            &(mol[start][i].type),
            &(mol[start][i].m),
            &(mol[start][i].r[0]),
            &(mol[start][i].r[1]),
            &(mol[start][i].r[2]),
            &(mol[start][i].status),
            &(mol[start][i].dis));
fclose(IN);
printf(HEADER);
printf("%d %g %g\n",
        atoms,
        pTstart,
        pXstart);
printf("%g %g %g %g\n",
        ms.total[start],
        ss.total[start],
        mss.total[start],
        BE[start]);
printf("%s %s %s %g\n",
        ms.name, ss.name, mss.name, mss.Var);
for (i = 0; i < atoms; i++)
    printf("%d %g %g %g %g %d %g\n",
            mol[start][i].type,
            mol[start][i].m,
            mol[start][i].r[0],
            mol[start][i].r[1],
            mol[start][i].r[2],
            mol[start][i].status,
            mol[start][i].dis);
printf("%g %g\n", moves, dEavg );

```

```

        return(0);
    }

/* write_config does the opposite of read_config. All positions etc have
 * of course been updated.
 */
void
write_config(int num, char *filename) {
    if ((OUT = fopen(filename, "w")) == NULL)
        printf("\nCan't open the file [%s].\n", filename);
    else {
        fprintf(OUT, "%d %g %g\n", atoms, max_moves, dEcrit );
        fprintf(OUT, "%g %g %g %g\n",
            pT, pTmin, dT, d2T);
        fprintf(OUT, "%g %g %g %g\n",
            pX, pXmin, dX, d2X);
        fprintf(OUT, "%12.8le %12.8le %12.8le %12.8le\n",
            ms.total[num], ss.total[num],
            mss.total[num], BE[num]);
        fprintf(OUT, "%s %s %s %12.8le\n",
            ms.name, ss.name, mss.name, mss.Var);
        for (i = 0; i < atoms; i++)
            fprintf(OUT, "%d %g %17.8le %17.8le %17.8le %d %g\n",
                mol[num][i].type,
                mol[num][i].m,
                mol[num][i].r[0],
                mol[num][i].r[1],
                mol[num][i].r[2],
                mol[num][i].status,
                mol[num][i].dis);
        fprintf(OUT, "%g %g\n", moves, dEavg );
    }
    fflush(OUT);
    fclose(OUT);
}

/* bru_write_config writes a file Dr. Brucat can read into his molecular
 * dynamics program.
 */
void
bru_write_config(int num, char *filename) {
    double d1,d2,d3,dummy;
    dummy=d1=d2=d3=0.0;

```

```

dummy=BE[num]*EV2CM;
if ((OUT = fopen(filename, "w")) == NULL) {
    printf("\nCan't open the file [%s].\n", outname);
} else {
    fprintf(OUT, "%d\n", atoms);
    fprintf(OUT, "%17.8le\n", dummy);
    for (i = 0; i < atoms; i++) {
        fprintf(OUT, "%17.8le %17.8le %17.8le\n",
            mol[num][i].r[0],
            mol[num][i].r[1],
            mol[num][i].r[2]);
        fprintf(OUT, "%17.8le %17.8le %17.8le\n%17.8le\n",
            d1,    d2,    d3,
            mol[num][i].m);
    }
}
fflush(OUT);
fclose(OUT);
}

void
alchemy_config(num, filename)
    int      num;
    char     filename[];
{
    /*      printf("Writing Alchemy File\n");      */

    if ((OUT = fopen(filename, "w")) == NULL)
        printf("\nCan't open the file [%s].\n", filename);
    else {
        fprintf(OUT, "%5d%8s%5d%s%(%)s%d\n", atoms,
            "ATOMS, ", atoms-1, " BONDS,    1 CHARGES, ",
            A[mol[num][0].type].n, A[mol[num][1].type].n, atoms-1);

        for (i=0; i<atoms; i++)
            fprintf(OUT, "%5d%1s%-2s%12.4lf%9.4lf%9.4lf\n", i+1, " ",
                A[mol[num][i].type].n, mol[num][i].r[0],
                mol[num][i].r[1], mol[num][i].r[2]);

        for (i=1; i<atoms; i++)
            fprintf(OUT, "%5d%6d%6d%s\n", i, 1, i+1, " SINGLE");
    }
    fflush(OUT);
}

```

```

        fclose(OUT);
    }

/* calc_mtotal returns the total mass of the cluster excluding any
 * dissociated atoms.
 */
double
calc_mtotal(int num) {
    double      ret = 0.0;

    for (i = 0; i < atoms; i++)
        if(mol[num][i].status != DISSOC) ret += mol[num][i].m;
    return(ret);
}

/* move_to_com moves the cluster to the center of mass */
void
move_to_com(int num) {
    int      i;

    for (i = 0; i < atoms; i++) {
        vect_smult(dummy, mol[num][i].r, mol[num][i].m);
        vect_add(com, com, dummy);
    }
    vect_sdiv(com, com, tmass[num]);
    for (i = 0; i < atoms; i++)
        vect_sub(mol[num][i].r, mol[num][i].r, com);
}

/* copy_config does that mol[new][i] = mol[old][i]... */
void
copy_config(int new, int old) {
    for (i = 0; i < atoms; i++) {
        vect_copy(mol[new][i].r, mol[old][i].r);
        mol[new][i].status = mol[old][i].status;
        mol[new][i].m = mol[old][i].m;
        mol[new][i].type = mol[old][i].type;
        mol[new][i].dis = mol[old][i].dis;
    }
}

/* temp_config moves the atoms depending upon the constraint. Presently
 * move the atoms at random any x,y,z represented by XYZ or move atoms

```



```

* keeping distance to ion constant represented by R_CONST. Also calc
* the BE for this temporary config.
*/
void
temp_config()
{
    double    scaling;

    attempts+=1.0;
    switch (constraint) {
    case XYZ:
        for (j = 0; j < atoms; j++) {
            if (mol[pres][j].status != FIXED) {
                mol[temp][j].r[0]=mol[pres][j].r[0]+Random(pX);
                mol[temp][j].r[1]=mol[pres][j].r[1]+Random(pX);
                mol[temp][j].r[2]=mol[pres][j].r[2]+Random(pX);
            }
        }
        break;
    case R_CONST:
        scaling = 1.0 + Random(pX);
        for (i = 0; i < atoms; i++)
            vect_smult(mol[temp][i].r, mol[pres][i].r, scaling);
        break;
    }
    BE[temp] = calc_potential(temp);
}

/* print_config(num) prints one of the configs: start, temp, pres, best, finish
* with all the current parameters.
*/
void
print_config(int num) {
    printf("\natoms= %d, max_moves= %g, moves= %g, dEcrit= %g\n",
           atoms, max_moves, moves, dEcrit);
    printf("pT= %g, pTmin= %g, dT= %g, d2T= %g\n",
           pT, pTmin, dT, d2T);
    printf("pX= %g, pXmin= %g, dX= %g, d2X= %g\n",
           pX, pXmin, dX, d2X);
    printf("%s %s %s %g\n", (ms.name), (ss.name), (mss.name), mss.Var);
    printf("%g + %g + %g = %g eV with dEavg= %g\n",
           ms.total[num], ss.total[num], mss.total[num], BE[num], dEavg);
    for (i = 0; i < atoms; i++) {

```

```

    vect_sub(va,mol[num][i].r,mol[num][0].r);
    mol[num][i].dis = vect_mag(va);
    printf("%d %g %g %g %g %d %g \n",
           mol[num][i].type,
           mol[num][i].m,
           mol[num][i].r[0],
           mol[num][i].r[1],
           mol[num][i].r[2],
           mol[num][i].status,
           mol[num][i].dis);
}
printf("tmass[%d] = %g\n",num,tmass[num]);

}

void calc_radial_distrib() {
    double      dumdum[3];
    int         distan;
    for(i=1;i<atoms;i++) {
        vect_sub(dumdum,mol[pres][i].r,mol[pres][0].r);
        distan = (int)(vect_mag(dumdum) *100.0);
        if (distan<1000) radial[distan] += 1.0;
    }
}

void calc_dipole(double *total,int num,int atoms) {
    double      mconst, dip[3], mx_d[3], xx_d[3], r3, va[3];
    int         i;

    mconst = QeSTAT * A_to_cm * 1e18;
    vect_0(total);
    vect_0(mx_d);
    vect_0(xx_d);

    for (i = 1; i < atoms; i++) {
        vect_sub(va, mol[num][i].r, mol[num][0].r);
        r3 = 1.0/(vect_mag(va));
        r3 *= r3 * r3;
        r3 *= A[(mol[num][i].type)].a;
        vect_smult(dip, va, r3);
        vect_add(xx_d, xx_d, dip);
    }
    vect_smult(xx_d, xx_d, mconst);
}

```

```

    vect_smult(mx_d, mol[num][0].r, mconst);

/*    vect_print("xx_d",xx_d,3);
    vect_print("mx_d",mx_d,3);
*/

    vect_add(total,mx_d,xx_d);
}

void calc_I(double **I,int num,int atoms) {
    double          **oI;
    int              nrot, i, j, k;

    oI=dmatrix(3,3);
    for (i = 0; i < 3; i++)
        for (j = 0; j < 3; j++)
            oI[i][j] = 0.0;
    for (i = 0; i < atoms; i++) {
        oI[0][0] += mol[num][i].m * (mol[num][i].r[1] * mol[num][i].r[1] +
mol[num][i].r[2] * mol[num][i].r[2]);
        oI[1][1] += mol[num][i].m * (mol[num][i].r[0] * mol[num][i].r[0] +
mol[num][i].r[2] * mol[num][i].r[2]);
        oI[2][2] += mol[num][i].m * (mol[num][i].r[0] * mol[num][i].r[0] +
mol[num][i].r[1] * mol[num][i].r[1]);
        for (j = 0; j < 3; j++) for (k = 0; k < 3; k++)
            if (j != k)
                oI[j][k] -= mol[num][i].m * mol[num][i].r[j] *
mol[num][i].r[k];
    }
    for (j = 0; j < 3; j++)
        for (k = 0; k < 3; k++)
            I[j][k] = oI[j][k] * A2_to_m2 * AMU;
}

void calc_Q(double **Q, int num,int atoms) {
    double          quad[3][3], U[3], R[3];
    int              i, j, k;

    for (j = 0; j < 3; j++)
        for (k = 0; k < 3; k++)
            Q[j][k] = 0.0;

    for (i = 1; i < atoms; i++) {
        vect_sub(R, mol[num][i].r, mol[num][0].r);

```

```

    vect_sdiv(U, R, (vect_mag(R)));

    for (j = 0; j < 3; j++) for (k = 0; k < 3; k++) {
        quad[j][k] = 3.0 * (mol[num][i].r[j] * U[k] + mol[num][i].r[k] *
U[j]);
        if (j == k)
            quad[j][j] -= 2.0 * vect_dot(mol[num][i].r, U);
    }

    for (j = 0; j < 3; j++) for (k = 0; k < 3; k++) {
        quad[j][k] *= (A[(mol[num][i].type)].a / vect_mag2(R));
        Q[j][k] += quad[j][k];
    }
}

for (j = 0; j < 3; j++) for (k = 0; k < 3; k++) {
    Q[j][k] += 3.0 * mol[num][0].r[j] * mol[num][0].r[k];
    if (j == k) Q[j][j] -= vect_mag2(mol[num][0].r);
}

for (j = 0; j < 3; j++)
    for (k = 0; k < 3; k++)
        Q[j][k] *= QeSTAT * A2_to_cm2 * 1e26;
}

void write_properties(double *rot, double *dipole, double **Q) {
    double dumdp;
    /*      printf("Writing Properties File\n");      */

    if ((DATA1 = fopen(dataname1, "w")) == NULL)
        printf("\nCan't open the file [%s].\n", dataname1);
    else {
        fprintf(DATA1, "%d\t%4.2lf\t%4.2lf\t%4.2lf\n",
            (atoms-1), rot[0], rot[1], rot[2]);
        fflush(DATA1);
        fclose(DATA1);
    }

    if ((DATA2 = fopen(dataname2, "w")) == NULL)
        printf("\nCan't open the file [%s].\n", dataname2);
    else {
        dumdp = vect_mag(dipole);
        fprintf(DATA2, "%d\t%4.2lf\t%4.2lf\t%4.2lf\t%4.2lf\n",

```

```

        (atoms-1), dipole[0], dipole[1], dipole[2], dumdp);
    fflush(DATA2);
    fclose(DATA2);
}

if ((DATA3 = fopen(dataname3, "w")) == NULL)
    printf("\nCan't open the file [%s].\n", dataname3);
else {
    fprintf(DATA3, "%d\t%4.2lf\t%4.2lf\t%4.2lf\t%4.2lf\t%4.2lf\n",
        (atoms-1), Q[0][0], Q[0][1], Q[0][2], Q[1][1], Q[1][2]);
    fflush(DATA3);
    fclose(DATA3);
}

if ((DATA4 = fopen(dataname4, "w")) == NULL)
    printf("\nCan't open the file [%s].\n", dataname4);
else {
    for(i=0;i<1000;i++)
        fprintf(DATA3, "%d  %g\n", i, radial[i]);
    fflush(DATA4);
    fclose(DATA4);
}

}

void calc_properties(int num) {
    int          n=3, nrot;
    double       dpmag;
    double       **I, **oI,
                 **Q, **oQ,
                 **U, **T,
                 *diagI,
                 *diagQ,
                 *rot,
                 *dipole;

    I = dmatrix(n,n);
    oI = dmatrix(n,n);
    Q = dmatrix(n,n);
    oQ = dmatrix(n,n);
    U = dmatrix(n,n);

```



```

T = dmatrix(n,n);

diagI = dvector(n);
dipole = dvector(n);
rot = dvector(n);

calc_I(I,num,atoms);
matrix_print("I", I, n, n);
jacobi(I, n, diagI, U, &nrot);
vect_print("diagI",diagI, n);
matrix_trans(T, U, n);
for (i = 0; i < 3; i++)
    rot[i] = 1000.0 * ROTCON / diagI[i];
vect_print("rot",rot,3);
calc_dipole(dipole,num,atoms);
vect_matrix(dipole, dipole, U, n);
vect_print("rotated dipole", dipole, n);
dpmag=vect_mag(dipole);
printf("d mag = %g\n\n", dpmag);

calc_Q(Q,num,atoms);
matrix_mult(oQ, Q, U, n);
matrix_mult(Q, T, oQ, n);
matrix_print("Q", Q, n, n);
write_properties(rot, dipole, Q);
}

/***** Statistics Utilities *****/
double Sum(double a[],int n) {
    double ret=0.0;
    for (i=0;i<n;i++) ret +=a[i];
    return(ret);
}

double Average(double a[],int n) {
    double ret=0.0;
    ret = Sum(a,n)/n;
    return(ret);
}

double Variance(double a[],int n) {
    double ret = 0.0, sum, xbar;

```

```

    sum = Sum(a,n);
    xbar = sum/n;
    for (i=0;i<n;i++) {
        sum = a[i] - xbar;
        ret += sum*sum;
    }
    return(ret);
}

double Std(double a[],int n) {
    double      ret = 0.0, sum, variance, xbar;

    sum = Sum(a,n);
    xbar = sum/n;
    for (i=0;i<n;i++) {
        sum = a[i] - xbar;
        variance += sum*sum;
    }
    ret = sqrt(variance)/n;
    return(ret);
}

double Prod(double a[],int n) {
    int      i;
    double prod=1.0;

    for (i=0;i<n;i++)
        prod*=a[i];
    return prod;
}

double FactN(int n) {
    double i;

    if (n==1) return (1);
    i = FactN(n-1)*n;
    return(i);
}

double Lpoly(int l, int m, double x ) {
    double      fact, pll, pmm, pmmp1, somx2;

```

```

int    i, ll;

pmm=1.0;
if (m>0) {
    somx2=sqrt((1.0-x)*(1.0+x));
    fact=1.0;
    for (i=0;i<m;i++) {
        pmm *= -fact*somx2;
        fact += 2.0;
    }
}
if (l==m)
    return pmm;
else {
    pmmp1 = x * (2*m+1)*pmm;
    if (l == (m+1))
        return pmmp1;
    else {
        for (ll=(m+2);ll<=l;ll++) {
            pll = (x*(2*ll-1)*pmmp1-(ll+m-1)*pmm)/(ll-m);
            pmm=pmmp1;
            pmmp1=pll;
        }
        return pll;
    }
}
}
→

```

```

/***** Functions
*****/

```

```

/* accept_temp is called if monte_carlo says the move was acceptable. It
 * copies mol[temp][i] to mol[pres][i] and if BE[pres] < BE[best] it also
 * copies mol[pres][i] to mol[best][i].
 */

```

```

void accept_temp() {
    moves += 1.0;
    move_to_com(temp);
    for (j = 0; j < atoms; j++)
        vect_copy(mol[pres][j].r, mol[temp][j].r);
    BE[pres]=BE[temp];
    ms.total[pres]=ms.total[temp];
}

```

```

mss.total[pres]=mss.total[temp];
ss.total[pres]=ss.total[temp];
if (BE[temp] < BE[best]) {
    for (j = 0; j < atoms; j++)
        vect_copy(mol[best][j].r, mol[temp][j].r);
    BE[best] = BE[temp];
    ms.total[best]=ms.total[temp];
    mss.total[best]=mss.total[temp];
    ss.total[best]=ss.total[temp];
}
}

int monte_carlo_average() {
    dE = BE[temp] - BE[pres];
    if ((dE < 0.0) || ( RandomPos(1.0) < exp(-dE/pT))) {
        accept_temp();
        return(1);
    } else return(0);
}

/* monte_carlo determines if a move was acceptable. If it was nsucc is
 * incremented else nfail is inc. If move was acceptable accept_temp() is
 * called. Function returns 1 if successful move and 0 otherwise.
 */
int monte_carlo() {
    attempts += 1.0;
    nattempts += 1.0;
    dE = BE[temp] - BE[pres];
    if ((dE < 0.0) || ( RandomPos(1.0) < exp(-dE/pT))) {
        dEtot+=dE;
        nsucc+=1.0;
        dEavg=dEtot/nsucc;
        if(dEavg < 0) dEavg*=-1.0;
        accept_temp();
        return(1);
    }
    else {
        nfail+=1.0;
        return(0);
    }
}

/* anneal determines the annealing cycle depending upon the ratio of nsucc to

```

```

* nfail. if the ratio is greater than 0.4 but less than 0.6 anneal_num is
* incremented until it is 200. Then at 200 pT is lowered by the fraction
* dT and anneal_num is reset. Raising and/or lowering of pT and/or pX are
* handled in this routine.
*/
void anneal() {
    ratio=nsucc/nfail;

/*    printf("ratio = %g, ",ratio);    */
    if((ratio > 0.4) && (ratio < 0.6)) {
        anneal_num+= 1.0;
        if(anneal_num > 200) {
            pT*=dT;
            anneal_num=1.0;
        }
        return;
    }
    if(ratio < 0.2) {
        if(ratio < 0.05) pX *= 0.1;
        else pX *= d2X;
        nsucc=nfail=nattempts=1.0;
        dEtot=0.0;
    } else if(ratio < 0.4) {
        pT *= dT;
        nsucc=nfail=nattempts=1.0;
        dEtot=0.0;
    }
    if(ratio > 0.6) {
        pT *= dT;
        pX /= dX;
        nsucc=nfail=nattempts=1.0;
        dEtot=0.0;
    }

/*    printf("temp= %g, step= %g\n\n",pT, pX);    */
}

/* check_mins checks to see if pT or pX are lower than their min value. If
* either are a new anneal cycle is begun with reset pT and pX and decreased
* dT and dX values.
*/
void check_mins() {

```



```

        if((pT<pTmin)|| (pX<pXmin)) {
            pT = pTstart*0.1;
            dT *= d2T;
            pX = pXstart*0.5;
            dX *= d2X;
            nsucc = nfail = nattempts = 1.0;
            dEtot = 0.0;
            pTmin *= 0.1;
            pXmin *= 0.1;
        }
    }

/* init_cluster assigns all three potentials ms.u, ss.u and mss.u. It also
 * makes 4 more copies of the starting config: temp, pres, best and finish.
 * It calculates the potential for each of these. It calculates the total
 * mass for each.
 */
void init_cluster() {
    int          num;

    assign_potentials();
    pT=pTstart;
    pX=pXstart;

    copy_config(1,start);
    copy_config(2,start);
    copy_config(3,start);
    copy_config(4,start);

    for(num=0;num<5;num++) BE[num]=calc_potential(num);
    for(num=0;num<5;num++) tmass[num]=calc_mtotal(num);

/*    for(num=0;num<5;num++) print_config(num);    */
}

/* init_program zeros all vectors prior to use. It also calls the atomic
 * element routines which assign atomic mass, symbol and polarizability.
 */
void init_program() {
    char *vecname;

    for(j=0;j<5;j++) {
        for(i=0;i<NATOMS;i++) {

```

```

        vect_0(mol[j][i].r);
    }
}

vect_0(va); vect_0(vb); vect_0(vab); vect_0(com); vect_0(dummy);

atomic_mass(); atomic_symbol(); atomic_alpha();

for(i=0;i<150;i++) radial[i]=0.0;
}

/* any_dissociation checks to see if any of the atoms in the molecule have
 * DISSOC status. This flag is set in the calc_potential where distances from
 * the central ion are calculated.
 */
int any_dissociation() {
    for(i=1;i<atoms;i++) if (mol[best][i].status==DISSOC) return(i);
    return(0);
}

/* calc_minimum does the work to minimize the cluster. It moves the atoms
 * with temp_config. It tests the config with monte_carlo. If monte_carlo
 * was good (ie returned 1) then it cycles m_cycle upto 1000 at which point
 * the best config is output by write_config(best,outname). It also controles
 * annealing by cycling a_cycle once nattempts is greater than 200. Once
 * critical values for dEavg less than dEcrit the program calculates the
 * equilb properties and outputs all necessary files.
 */
void calc_minimum() {
    temp_config();
    if (monte_carlo()) {
        m_cycle++;
        m_cycle %= 1000;
        if (!m_cycle) {
            print_config(best);
            if (any_dissociation()) {
                pT = pTmin * 10.0;
                pX = pXstart * 5.0;
                nsucc = nfail = nattempts = 1.0;
                dEtot = 0.0;
            }
            write_config(best,outname);
        }
    }
}

```

```

    }
}
if (nattempts > 200) {
    a_cycle++;
    a_cycle %= 10;
    if(!a_cycle) anneal();
    min_cycle++;
    min_cycle %= 500;
    if(!min_cycle) check_mins();
}
if((moves>max_moves)&&(dEavg<dEcrit)) {
    error=done=TRUE;
    write_config(best,outname);
}
}

/***** Main Program Logic *****/
void main(int argc,char **argv) {
    do {
        printf(HEADER);
        strcpy(error_type,"normal termination");

        if (argc == 2) {
            strcpy(inname, argv[1]);
            strncpy(outname, inname, (strlen(inname)-3) );
            strcpy(bruname, outname);
            strcat(bruname, ".bru");
            strcpy(dataname1, outname);
            strcat(dataname1, ".rot");
            strcpy(dataname2, outname);
            strcat(dataname2, ".dip");
            strcpy(dataname3, outname);
            strcat(dataname3, ".qua");
            strcpy(dataname4, outname);
            strcat(dataname4, ".dis");
            strcpy(alchname, outname);
            strcat(alchname, ".mol");
            strcat(outname, ".out");
        }
        init_program();
        if(done=error=read_config(inname)) {
            strcpy(error_type, "unreadable file");

```

```
        break;
    }
    if(done) break;
    init_cluster();
    do {
        calc_minimum();
    } while (!done);
} while (!error);
if(error) ra_error(error,error_type);
}
```

Included Files

```
/* Various scientific constants and conversions...
```

```
*
```

```
* Program Name:    <sciconst.h> V2.1
```

```
* Author:         Robert L. Asher
```

```
* Employer:       University of Florida
```

```
* Original Date:   November 4, 1990
```

```
* Latest Revision: February 9, 1994
```

```
*
```

```
*/
```

```
#ifndef __SCICONST_H
```

```
#define __SCICONST_H
```

```
extern const double Pi          = 4.0 * atan(1.0);
```

```
extern const double Pi2        = Pi * Pi;
```

```
extern const double PiOver2    = Pi / 2.0;
```

```
extern const double PiOver4    = Pi / 4.0;
```

```
extern const double TwoPi      = Pi * 2.0;
```

```
extern const double FourPi     = Pi * 4.0;
```

```
extern const double Hjoules     = 6.626176e-34;
```

```
extern const double Hjoules2    = Hjoules * Hjoules;
```

```
extern const double HBarjoules  = Hjoules / TwoPi;
```

```
extern const double HBarjoules2= Hjoules / TwoPi;
```

```
extern const double Herg       = Hjoules * 1e7;
```

```
extern const double HBarerg    = Herg / TwoPi;
```

```
extern const double Hcm        = 12.899226;
```

```
extern const double HBarcm     = Hcm / TwoPi;
```

```
extern const double Cm         = 299792458.0;
```

```
extern const double Ccm        = Cm * 100.0;
```

```
extern const double Avagadro    = 6.022045e23;
```

```
extern const double Qe         = 1.6021892e-19;
```

```
extern const double Qe2        = Qe * Qe;
```

```
extern const double AMU        = 1.6605655e-27;
```

```
extern const double Kb_joules  = 1.380662e-23;
```

```
extern const double Kb_erg     = Kb_joules*1e7;
```

```
extern const double Kb_AmuAps  = Kb_joules*1e-4/AMU;
```

```
extern const double ElectronM  = 9.109534e-31;
```

```
extern const double EPo        = 8.854187818e-12;
```

```
extern const double K          = FourPi * EPo;
```

```
extern const double QeStat     = Qe * Cm * 10.0;
```



```

extern const double QeStat2 = QeStat * QeStat;
extern const double BohrRadius = (K*HBarjoules2)/(ElectronM*Qe);
extern const double A_to_m = 1e-10;
extern const double A2_to_m2 = 1e-20;
extern const double A3_to_m3 = 1e-30;
extern const double A_to_cm = 1e-8;
extern const double A2_to_cm2 = 1e-16;
extern const double A3_to_cm3 = 1e-24;
extern const double cm_to_A = 1e8;
extern const double cm2_to_A2 = 1e16;
extern const double cm3_to_A3 = 1e24;
extern const double erg_to_eV = 6.241460122e11;
extern const double eV_to_erg = 1.6021892e-12;
extern const double J_to_AmuAps = 1e-4 / AMU;
extern const double eV_to_AmuAps = 1e-4 * Qe / AMU;
extern const double J_to_wave = 1.0/1.986e-23;
#endif

```

```

/* C++ Element File, which contains:
 * Element Class with mass, polarizability, symbol, and name.
 *
 * Program Name: <element.h> V1.0
 * Author: Robert L. Asher
 * Employer: University of Florida
 * Original Date: November 4, 1990
 * Latest Revision: July 7, 1993
 *
 * Internal units are (amu) and (angstroms) unless stated otherwise.
 *
 */

```

```

class Element {
private:
    void      Mass(int),           // atomic mass
              Polarizability(int), // atomic polarizability
              Symbol(int),         // atomic symbol
              Name(int);           // atomic name

public:
    double    mass,
              alpha;
    char      symbol[80],

```

```

        name[80];
void      Assign(char* id),
          Assign(int);
Element& operator=(const Element&);
};

Element& Element::operator=(const Element& copy) {
    if(mass != copy.mass) {
        mass=copy.mass;
        alpha=copy.alpha;
        strcpy(symbol,copy.symbol);
        strcpy(name,copy.name);
    }
    return *this;
}

void Element::Assign(char* id) {
    int num;
    for(num=1;num<101;num++) {
        Symbol(num);
        if(!strncmp(id,symbol,2)) break;
    }
    Name(num);
    Polarizability(num);
}

void Element::Assign(int num) {
    Symbol(num);
    Name(num);
    Polarizability(num);
}

void Element::Mass(int num) {
    switch(num) {
        case 1:mass = 1.00794;break; case 2:mass = 4.002602;break;
        case 3:mass = 6.941;break;   case 4:mass = 9.012182;break;
        case 5:mass = 10.811;break;  case 6:mass = 12.011;break;
        case 7:mass = 14.00674;break; case 8:mass = 15.9994;break;
        case 9:mass = 18.9984032;break; case 10:mass = 20.1797;break;
        case 11:mass = 22.989768;break; case 12:mass = 24.3050;break;
        case 13:mass = 26.981539;break; case 14:mass = 28.0855;break;
        case 15:mass = 30.973762;break; case 16:mass = 32.066;break;
        case 17:mass = 35.4527;break;  case 18:mass = 39.948;break;
    }
}

```

```

case 19:mass = 39.0983;break;      case 20:mass = 40.078;break;
case 21:mass = 44.955910;break;    case 22:mass = 47.88;break;
case 23:mass = 50.9415;break;      case 24:mass = 51.9961;break;
case 25:mass = 54.93805;break;     case 26:mass = 55.847;break;
case 27:mass = 58.93320;break;     case 28:mass = 58.69;break;
case 29:mass = 63.546;break; case 30:mass = 65.39;break;
case 31:mass = 69.723;break; case 32:mass = 72.61;break;
case 33:mass = 74.92159;break;     case 34:mass = 78.96;break;
case 35:mass = 79.904;break; case 36:mass = 83.80;break;
case 37:mass = 85.4678;break;      case 38:mass = 87.62;break;
case 39:mass = 88.90585;break;     case 40:mass = 91.224;break;
case 41:mass = 92.90638;break;     case 42:mass = 95.94;break;
case 43:mass = 98.9063;break;      case 44:mass = 101.07;break;
case 45:mass = 102.90550;break;    case 46:mass = 106.42;break;
case 47:mass = 107.8682;break;     case 48:mass = 112.411;break;
case 49:mass = 114.82;break; case 50:mass = 118.710;break;
case 51:mass = 121.75;break; case 52:mass = 127.60;break;
case 53:mass = 126.90447;break;    case 54:mass = 131.29;break;
case 55:mass = 132.90543;break;    case 56:mass = 137.327;break;
case 57:mass = 138.9055;break;     case 58:mass = 140.115;break;
case 59:mass = 140.90765;break;    case 60:mass = 144.24;break;
case 61:mass = 146.9151;break;     case 62:mass = 150.36;break;
case 63:mass = 151.965;break;      case 64:mass = 157.25;break;
case 65:mass = 158.92534;break;    case 66:mass = 162.50;break;
case 67:mass = 164.93032;break;    case 68:mass = 167.26;break;
case 69:mass = 168.93421;break;    case 70:mass = 173.04;break;
case 71:mass = 174.967;break;      case 72:mass = 174.49;break;
case 73:mass = 180.9479;break;     case 74:mass = 183.85;break;
case 75:mass = 186.207;break;      case 76:mass = 190.2;break;
case 77:mass = 192.22;break; case 78:mass = 195.08;break;
case 79:mass = 196.96654;break;    case 80:mass = 200.59;break;
case 81:mass = 204.3833;break;     case 82:mass = 207.2;break;
case 83:mass = 208.98037;break;    case 84:mass = 208.9824;break;
case 85:mass = 209.9871;break;     case 86:mass = 222.0176;break;
case 87:mass = 223.0197;break;     case 88:mass = 226.0254;break;
case 89:mass = 227.0278;break;     case 90:mass = 232.0381;break;
case 91:mass = 231.0359;break;     case 92:mass = 238.0289;break;
case 93:mass = 237.0482;break;     case 94:mass = 244.0642;break;
case 95:mass = 243.0614;break;     case 96:mass = 247.0703;break;
case 97:mass = 247.0703;break;     case 98:mass = 251.0796;break;
case 99:mass = 252.0829;break;     case 100:mass = 257.0951;break;
};

```

```

}

```

```
void Element::Symbol(int num) {  
    switch(num) {  
        case 1:strcpy(symbol,"H\0");break;  
        case 2:strcpy(symbol,"He\0");break;  
        case 3:strcpy(symbol,"Li\0");break;  
        case 4:strcpy(symbol,"Be\0");break;  
        case 5:strcpy(symbol,"B\0");break;  
        case 6:strcpy(symbol,"C\0");break;  
        case 7:strcpy(symbol,"N\0");break;  
        case 8:strcpy(symbol,"O\0");break;  
        case 9:strcpy(symbol,"F\0");break;  
        case 10:strcpy(symbol,"Ne\0");break;  
        case 11:strcpy(symbol,"Na\0");break;  
        case 12:strcpy(symbol,"Mg\0");break;  
        case 13:strcpy(symbol,"Al\0");break;  
        case 14:strcpy(symbol,"Si\0");break;  
        case 15:strcpy(symbol,"P\0");break;  
        case 16:strcpy(symbol,"S\0");break;  
        case 17:strcpy(symbol,"Cl\0");break;  
        case 18:strcpy(symbol,"Ar\0");break;  
        case 19:strcpy(symbol,"K\0");break;  
        case 20:strcpy(symbol,"Ca\0");break;  
        case 21:strcpy(symbol,"Sc\0");break;  
        case 22:strcpy(symbol,"Ti\0");break;  
        case 23:strcpy(symbol,"V\0");break;  
        case 24:strcpy(symbol,"Cr\0");break;  
        case 25:strcpy(symbol,"Mn\0");break;  
        case 26:strcpy(symbol,"Fe\0");break;  
        case 27:strcpy(symbol,"Co\0");break;  
        case 28:strcpy(symbol,"Ni\0");break;  
        case 29:strcpy(symbol,"Cu\0");break;  
        case 30:strcpy(symbol,"Zn\0");break;  
        case 31:strcpy(symbol,"Ga\0");break;  
        case 32:strcpy(symbol,"Ge\0");break;  
        case 33:strcpy(symbol,"As\0");break;  
        case 34:strcpy(symbol,"Se\0");break;  
        case 35:strcpy(symbol,"Br\0");break;  
        case 36:strcpy(symbol,"Kr\0");break;  
        case 37:strcpy(symbol,"Rb\0");break;  
        case 38:strcpy(symbol,"Sr\0");break;  
        case 39:strcpy(symbol,"Y\0");break;  
        case 40:strcpy(symbol,"Zr\0");break;  
        case 41:strcpy(symbol,"Nb\0");break;
```



```
case 42: strcpy(symbol, "Mo\0"); break;
case 43: strcpy(symbol, "Tc\0"); break;
case 44: strcpy(symbol, "Ru\0"); break;
case 45: strcpy(symbol, "Rh\0"); break;
case 46: strcpy(symbol, "Pd\0"); break;
case 47: strcpy(symbol, "Ag\0"); break;
case 48: strcpy(symbol, "Cd\0"); break;
case 49: strcpy(symbol, "In\0"); break;
case 50: strcpy(symbol, "Sn\0"); break;
case 51: strcpy(symbol, "Sb\0"); break;
case 52: strcpy(symbol, "Te\0"); break;
case 53: strcpy(symbol, "I\0"); break;
case 54: strcpy(symbol, "Xe\0"); break;
case 55: strcpy(symbol, "Cs\0"); break;
case 56: strcpy(symbol, "Ba\0"); break;
case 57: strcpy(symbol, "La\0"); break;
case 58: strcpy(symbol, "Ce\0"); break;
case 59: strcpy(symbol, "Pr\0"); break;
case 60: strcpy(symbol, "Nd\0"); break;
case 61: strcpy(symbol, "Pm\0"); break;
case 62: strcpy(symbol, "Sm\0"); break;
case 63: strcpy(symbol, "Eu\0"); break;
case 64: strcpy(symbol, "Gd\0"); break;
case 65: strcpy(symbol, "Tb\0"); break;
case 66: strcpy(symbol, "Dy\0"); break;
case 67: strcpy(symbol, "Ho\0"); break;
case 68: strcpy(symbol, "Er\0"); break;
case 69: strcpy(symbol, "Tm\0"); break;
case 70: strcpy(symbol, "Yb\0"); break;
case 71: strcpy(symbol, "Lu\0"); break;
case 72: strcpy(symbol, "Hf\0"); break;
case 73: strcpy(symbol, "Ta\0"); break;
case 74: strcpy(symbol, "W\0"); break;
case 75: strcpy(symbol, "Re\0"); break;
case 76: strcpy(symbol, "Os\0"); break;
case 77: strcpy(symbol, "Ir\0"); break;
case 78: strcpy(symbol, "Pt\0"); break;
case 79: strcpy(symbol, "Au\0"); break;
case 80: strcpy(symbol, "Hg\0"); break;
case 81: strcpy(symbol, "Tl\0"); break;
case 82: strcpy(symbol, "Pb\0"); break;
case 83: strcpy(symbol, "Bi\0"); break;
case 84: strcpy(symbol, "Po\0"); break;
```



```

case 85:strcpy(symbol,"At\0");break;
case 86:strcpy(symbol,"Rn\0");break;
case 87:strcpy(symbol,"Fr\0");break;
case 88:strcpy(symbol,"Ra\0");break;
case 89:strcpy(symbol,"Ac\0");break;
case 90:strcpy(symbol,"Th\0");break;
case 91:strcpy(symbol,"Pa\0");break;
case 92:strcpy(symbol,"U\0");break;
case 93:strcpy(symbol,"Np\0");break;
case 94:strcpy(symbol,"Pu\0");break;
case 95:strcpy(symbol,"Am\0");break;
case 96:strcpy(symbol,"Cm\0");break;
case 97:strcpy(symbol,"Bk\0");break;
case 98:strcpy(symbol,"Cf\0");break;
case 99:strcpy(symbol,"Es\0");break;
case 100:strcpy(symbol,"Fm\0");break;
};
}

void Element::Name(int num) {
    switch(num) {
        case 1:strcpy(name,"Hydrogen\0");break;
        case 2:strcpy(name,"Helium\0");break;
        case 3:strcpy(name,"Lithium\0");break;
        case 4:strcpy(name,"Beryllium\0");break;
        case 5:strcpy(name,"Boron\0");break;
        case 6:strcpy(name,"Carbon\0");break;
        case 7:strcpy(name,"Nitrogen\0");break;
        case 8:strcpy(name,"Oxygen\0");break;
        case 9:strcpy(name,"Fluorine\0");break;
        case 10:strcpy(name,"Neon\0");break;
        case 11:strcpy(name,"Sodium\0");break;
        case 12:strcpy(name,"Magnesium\0");break;
        case 13:strcpy(name,"Aluminium\0");break;
        case 14:strcpy(name,"Silicon\0");break;
        case 15:strcpy(name,"Phosphorus\0");break;
        case 16:strcpy(name,"Sulfur\0");break;
        case 17:strcpy(name,"Chlorine\0");break;
        case 18:strcpy(name,"Argon\0");break;
        case 19:strcpy(name,"Potassium\0");break;
        case 20:strcpy(name,"Calcium\0");break;
        case 21:strcpy(name,"Scandium\0");break;
        case 22:strcpy(name,"Titanium\0");break;
    }
}

```

```
case 23:strcpy(name,"Vanadium\0");break;
case 24:strcpy(name,"Chromium\0");break;
case 25:strcpy(name,"Manganese\0");break;
case 26:strcpy(name,"Iron\0");break;
case 27:strcpy(name,"Cobalt\0");break;
case 28:strcpy(name,"Nickel\0");break;
case 29:strcpy(name,"Copper\0");break;
case 30:strcpy(name,"Zinc\0");break;
case 31:strcpy(name,"Gallium\0");break;
case 32:strcpy(name,"Germanium\0");break;
case 33:strcpy(name,"Arsenic\0");break;
case 34:strcpy(name,"Selenium\0");break;
case 35:strcpy(name,"Bromine\0");break;
case 36:strcpy(name,"Krypton\0");break;
case 37:strcpy(name,"Rubidium\0");break;
case 38:strcpy(name,"Strontium\0");break;
case 39:strcpy(name,"Yttrium\0");break;
case 40:strcpy(name,"Zirconium\0");break;
case 41:strcpy(name,"Niobium\0");break;
case 42:strcpy(name,"Molybdenum\0");break;
case 43:strcpy(name,"Technetium\0");break;
case 44:strcpy(name,"Ruthenium\0");break;
case 45:strcpy(name,"Rhodium\0");break;
case 46:strcpy(name,"Palladium\0");break;
case 47:strcpy(name,"Silver\0");break;
case 48:strcpy(name,"Cadmium\0");break;
case 49:strcpy(name,"Indium\0");break;
case 50:strcpy(name,"Tin\0");break;
case 51:strcpy(name,"Antimony\0");break;
case 52:strcpy(name,"Tellurium\0");break;
case 53:strcpy(name,"Iodine\0");break;
case 54:strcpy(name,"Xenon\0");break;
case 55:strcpy(name,"Caesium\0");break;
case 56:strcpy(name,"Barium\0");break;
case 57:strcpy(name,"Lanthanum\0");break;
case 58:strcpy(name,"Cerium\0");break;
case 59:strcpy(name,"Praseodymium\0");break;
case 60:strcpy(name,"Neodymium\0");break;
case 61:strcpy(name,"Promethium\0");break;
case 62:strcpy(name,"Samarium\0");break;
case 63:strcpy(name,"Europium\0");break;
case 64:strcpy(name,"Gadolinium\0");break;
case 65:strcpy(name,"Terbium\0");break;
```

```

case 66:strcpy(name,"Dysprosium\0");break;
case 67:strcpy(name,"Holmium\0");break;
case 68:strcpy(name,"Erbium\0");break;
case 69:strcpy(name,"Thulium\0");break;
case 70:strcpy(name,"Ytterbium\0");break;
case 71:strcpy(name,"Lutetium\0");break;
case 72:strcpy(name,"Hafnium\0");break;
case 73:strcpy(name,"Tantalum\0");break;
case 74:strcpy(name,"Tungsten\0");break;
case 75:strcpy(name,"Rhenium\0");break;
case 76:strcpy(name,"Osmium\0");break;
case 77:strcpy(name,"Iridium\0");break;
case 78:strcpy(name,"Platinum\0");break;
case 79:strcpy(name,"Gold\0");break;
case 80:strcpy(name,"Mercury\0");break;
case 81:strcpy(name,"Thallium\0");break;
case 82:strcpy(name,"Lead\0");break;
case 83:strcpy(name,"Bismuth\0");break;
case 84:strcpy(name,"Polonium\0");break;
case 85:strcpy(name,"Astatine\0");break;
case 86:strcpy(name,"Radon\0");break;
case 87:strcpy(name,"Francium\0");break;
case 88:strcpy(name,"Radium\0");break;
case 89:strcpy(name,"Actinium\0");break;
case 90:strcpy(name,"Thorium\0");break;
case 91:strcpy(name,"Protactinium\0");break;
case 92:strcpy(name,"Uranium\0");break;
case 93:strcpy(name,"Neptunium\0");break;
case 94:strcpy(name,"Plutonium\0");break;
case 95:strcpy(name,"Americium\0");break;
case 96:strcpy(name,"Curium\0");break;
case 97:strcpy(name,"Berkelium\0");break;
case 98:strcpy(name,"Californium\0");break;
case 99:strcpy(name,"Einsteinium\0");break;
case 100:strcpy(name,"Fermium\0");break;
};

```

```

}

```

```

void Element::Polarizability(int num) {
    switch(num) {
        case 2:alpha = 0.206;break;
        case 10:alpha = 0.397;break;
        case 18:alpha = 1.66;break;
    }
}

```

```

        case 36:alpha = 2.52;break;
        case 54:alpha = 4.11;break;
    };
}

/* C++ Analytic Potential Include File, which contains:
 * - The Potential Class
 * - Various analytic potentials and their gradients (if easily derived)
 * - Some standard parameters and a way to read in non standard ones
 *
 * Program Name:    <pot.h> V1.1
 * Author:          Robert L. Asher
 * Employer:        University of Florida
 * Original Date:    November 4, 1990
 * Latest Revision:  July 7, 1993
 *
 * Internal units are (amu), (angstroms) and (ps) unless stated otherwise.
 *
 */

```

```

class Potential {
public:
    DoubleVec    C,
                r;
    double       d,                // distance
                De,
                Re,
                We,
                Mu;

    Potential();                    // Constructor
    ~Potential();                  // Destructor
    char    name[80];
    void    Assign(),
            UPlot(double,double,double),
            gUPlot(double,double,double),
            Read(),
            Report();

    double Zero(double r) {return(0.0*r);};
    double Zero(double r1 ,double r2) {return(0.0*r1*r2);};

    double

```



```

        u6_4(double),           // Lennard Jones 6-4
        u8_4(double),           // Lennard Jones 8-4
        u8_6_4(double),         // Lennard Jones 8-6-4
        u12_6(double),          // Lennard Jones 12-6
        uB_M(double),           // Born Maier
        uH_O(double),           // Harmonic Oscilator
        uMorse(double);         // Morse

double (Potential::*pmf_U)(double);
double U(double r) {return(this->*pmf_U)(r);};

double
        g6_4(double),           // Lennard Jones 6-4
        g8_4(double),           // Lennard Jones 8-4
        g8_6_4(double),         // Lennard Jones 8-6-4
        g12_6(double),          // Lennard Jones 12-6
        gB_M(double),           // Born Maier
        gH_O(double),           // Harmonic Oscilator
        gMorse(double);         // Morse

double (Potential::*pmf_gU)(double);
double gU(double r) {return(this->*pmf_gU)(r);};

double
        i6_4(double,double),     // Lennard Jones 6-4
        i8_4(double,double),     // Lennard Jones 8-4
        i8_6_4(double,double),   // Lennard Jones 8-6-4
        i12_6(double,double),    // Lennard Jones 12-6
        iB_M(double,double),     // Born Maier
        iH_O(double,double),     // Harmonic Oscilator
        iMorse(double,double);   // Morse

double (Potential::*pmf_iU)(double,double);
double iU(double R1, double R2) {return(this->*pmf_iU)(R1,R2);};
};

/***** Potential Member Functions
*****/
void Potential::Potential() {
    r.resize(20);
    C.resize(20);
    De=We=Re=Mu=0.0;
    for(int i=0;i<20;i++ ) C(i)=r(i)=0.0;

```



```

        strcpy(name, "\0");
    }

Potential::~Potential() {
    Report();
}

void Potential::Report() {
    cout << name << "\n";
    if(De !=0.0) cout << "De " << De << "\n";
    if(Re !=0.0) cout << "Re " << Re << "\n";
    if(We !=0.0) cout << "We " << We << "\n";
    if(Mu !=0.0) cout << "Mu " << Mu << "\n";
    for(int i=0;i<20;i++) {
        if(C(i) != 0.0) cout << "C" << i << " " << C(i) << "\n";
    }
}

void Potential::Read() {
    char dummy[80];
    cin >> dummy;
    cin >> name;
    cin >> dummy;
    if(strcmp(dummy, "None")) {
        cout << "Fucked up!\n";
        cin >> De;
        cin >> Re;
        cin >> Mu;
        cin >> C;
    }
    Assign();
    Report();
}

void Potential::UPlot(double start, double finish, double step) {
    for(double x=start;x<finish;x+=step) cout << x << " " << U(x) << "\n";
}

void Potential::gUPlot(double start, double finish, double step) {
    for(double x=start;x<finish;x+=step) cout << x << " " << gU(x) << "\n";
}

```

```

void Potential::Assign() {
    if(!strcmp(name,"VAr8_4")) {
        pmf_U      = &Potential::u8_4;
        pmf_gU      = &Potential::g8_4;
        pmf_iU      = &Potential::i8_4;
        C(4)  = 1.66 * QeStat2 * erg_to_eV * 1e8 / 2.0;
        C(8)  = (C(4) * C(4))/(4.0 * 0.381);
        C(4)  *= eV_to_AmuAps; // convert to (amu)(A)^2/(ps)^2
        C(8)  *= eV_to_AmuAps;
        C(9)  = -8.0*C(8);
        C(5)  = -4.0*C(4);
        C(3)  = -C(4)/3.0;
        C(7)  = -C(8)/7.0;
    } else if(!strcmp(name,"ArAr12_6")) {
        pmf_U      = &Potential::u12_6;
        pmf_gU      = &Potential::g12_6;
        pmf_iU      = &Potential::i12_6;
        C(6)  = 3.41 * 3.41 * 3.41;
        C(6)  *= C(6);
        C(12) = C(6)*C(6);
        C(6)  *= 4.0 * 0.01207 * eV_to_AmuAps;
        C(12) *= 4.0 * 0.01207 * eV_to_AmuAps;
        C(13) = -12.0*C(12);
        C(7)  = -6.0*C(6);
        C(5)  = -C(6)/5.0;
        C(11) = -C(12)/11.0;
    } else {
        pmf_U=&Potential::Zero;
        pmf_gU=&Potential::Zero;
        pmf_iU=&Potential::Zero;
    }
}

double Potential::u6_4(double d) {
    r(2) = d * d;
    r(4) = r(2) * r(2);
    r(6) = r(2) * r(4);
    return((C(6)/r(6))-(C(4)/r(4)));
}

double Potential::u8_4(double d) {
    r(4) = d * d;
    r(4) *= r(4);

```

```

    r(8) = r(4) * r(4);
    return((C(8)/r(8)) - (C(4)/r(4)));
}

```

```

double Potential::u8_6_4(double d) {
    r(8) = d * d;
    r(4) = r(8) * r(8);
    r(6) = r(4) * r(8);
    r(8) = r(4) * r(4);
    return((C(8)/r(8))-(C(6)/r(6))-(C(4)/r(4)));
}

```

```

double Potential::u12_6(double d) { // The Lennard Jones 12-6 potential
    r(6) = d * d * d;
    r(6) *= r(6);
    r(12) = r(6) * r(6);
    return((C(12)/r(12)) - (C(6)/r(6)));
}

```

```

double Potential::uB_M(double d) {
    double ret;
    r(4) = d * d;
    r(4) *= r(4);
    ret = -d/C(0);
    ret = exp(ret);
    ret *= C(1);
    ret -= (C(4)/r(4));
    return(ret);
}

```

```

double Potential::uH_O(double d) { // V=(kx^2)/2
    r(2) = (d-Re);
    r(2) *= r(2);
    return((0.5 * C(0) * r(2)) + De);
}

```

```

double Potential::uMorse(double d) { // V=De(1-e^B(r-Re))^2
    r(0) = C(0) * (Re - d);
    r(2) = 1.0 - exp(r(0));
    r(2) *= r(2);
    return(De * r(2));
}

```

```
double Potential::g6_4(double d) {
    r(2) = d*d;
    r(4) = r(4) * r(4);
    r(5) = r(4) * d;
    r(7) = r(5) * r(2);
    return((C(7)/r(7))-(C(5)/r(5)));
}
```

```
double Potential::g8_4(double d) { // The Lenard Jones 8-4 gradient
    r(4) = d*d;
    r(4) *= r(4);
    r(5) = r(4) * d;
    r(9) = r(4) * r(5);
    return((C(9)/r(9)) - (C(5)/r(5)));
}
```

```
double Potential::g12_6(double d) { // The Lenard Jones 12-6 gradient
    r(6) = d * d * d;
    r(6) *= r(6);
    r(7) = r(6) * d;
    r(13) = r(6) * r(7);
    return((C(13)/r(13)) - (C(7)/r(7)));
}
```

```
double Potential::g8_6_4(double d) {
    r(2) = d * d;
    r(4) = r(2) * r(2);
    r(5) = r(4) * d;
    r(7) = r(5) * r(2);
    r(9) = r(4) * r(5);
    return((C(9)/r(9))-(C(7)/r(7))-(C(5)/r(5)));
}
```

```
double Potential::i8_4(double R1, double R2) {
    double ret=0.0;
    r(2) = R1 * R1;
    r(3) = r(2) * R1;
    r(7) = r(3) * r(3) * R1;
    ret = (C(7)/r(7)) - (C(3)/r(3));
    r(2) = R2 * R2;
    r(3) = r(2) * R2;
    r(7) = r(3) * r(3) * R2;
    ret -= (C(7)/r(7)) - (C(3)/r(3));
}
```

```

        return(ret);
    }

double Potential::i12_6(double R1, double R2) {
    double ret=0.0;

    r(2) = R1 * R1;
    r(5) = r(2) * r(2) * R1;
    r(11) = r(5) * r(5) * R1;
    ret = (C(5)/r(5)) - (C(11)/r(11));
    r(2) = R2 * R2;
    r(5) = r(2) * r(2) * R2;
    r(11) = r(5) * r(5) * R2;
    ret -= (C(5)/r(5)) - (C(11)/r(11));
    return(ret);
}

/* C++ Statistical Class:
 *
 * Program Name:    <statist.h> V1.0
 * Author:         Robert L. Asher
 * Employer:       University of Florida
 * Original Date:   November 4, 1990
 * Latest Revision: July 7, 1993
 *
 */

struct Statistical {
    DoubleVec    Data;
    long         Size;
    double       Avg,
                Var,
                Val,
                Set,
                Std,
                ATol,
                STol;
    void         Report(char *),
                Read();
    Statistical();
};

Statistical::Statistical() {

```



```
Avg=Std=Val=Var=Set=ATol=STol=0.0;
Size=0;
}

void Statistical::Read() {
    cin >> Size;
    cin >> Set;
    cin >> ATol;
    cin >> STol;
    Data.resize(Size);
}

void Statistical::Report(char *name) {
    cout << name << ":" << endl;
    cout << "Set=" << Set << " Avg=" << Avg << " Val=" << Val << "\n"
        << "Size=" << Size << " ATol=" << ATol << " STol=" << STol
        << " Std=" << Std << "\n";
}
```

Canonical and Microcanonical Trajectory Program

```

/* C++ Program to do either canonical or microcanonical molecular dynamics.
* Portions addapted from a C program by Philip J. Brucat.
*
* Program compiles under DOS Borland's C++ 3.1 with Rogue Wave Math.h++ 5.1.
*
* Program Name:    <can.cpp> V3.0a
* Author:          Robert L. Asher
* Employer:        University of Florida
* Original Date:    October 1, 1992
* Revision Date:    November 10, 1994
*
* Differences from last version:    should calculate radial distribution
*
* Internal units are (amu),(angstroms) and (ps) unless stated otherwise.
* Recall these conversions:
*      1 (J) = 6.241460122e18      (eV)                = 1 / Qe
*      1 (J) = 6.0220449e22      (Amu)(A)^2/(ps)^2    = 1e-4 / AMU
*      1 (eV) = 9648.4553      (Amu)(A)^2/(ps)^2    = 1e-4 * Qe / AMU
*
*/

const char *BANNER = "<can.cpp>\tV3.0a \tNovember 10, 1994\tRobert L. Asher\n";

/***** Standard C++ Include Files
*****/
#include <stdio.h>                // C++ standard I/O routines
#include <stdlib.h>               // C++ standard library
#include <string.h>               // C++ string routines
#include <math.h>                 // C++ math routines
#include <values.h>               // C++ constants
#include <ctype.h>                // C++ types
#include <time.h>                 // C++ time classes
#include <fstream.h>

/***** Rogue Wave LinPack.h++ Include Files
*****/
#include "rw\dvec.h"              // Rogue Wave vector routines
#include "rw\rstream.h"           // Rogue Wave stream routines
#include "rw\dgenmat.h"           // Rogue Wave matrix routines
#include "rw\dgenfct.h"           // Rogue Wave lin alg routines

```

```

#include <statist.h>
#include <element.h>                // Element Class and Functions
#include <sciconst.h>               // Scientific Consts & Convs
#include <pot.h>                    // Potential Class and Fns
#include <timestamp.h>

/***** Global Definitions and Declarations *****/
int TESTING;

const int      MAX_NUM = MAXSHORT/2,
              MAX_POS = MAXSHORT;

fstream        ConfigFile,
              NeighborFile,
              RadialFile,
              LogFile,
              OutputFile;

char           ConfigName[80],
              NeighborName[80],
              RadialName[80],
              LogName[80],
              OutputName[80];

char           JunkText[80];

DoubleVec      VectorZero(3,0.0);
DoubleGenMat    MatrixZero(3,3,0.0);

char const     S[5]          = " \0";      // a space ie.) cout << S...

/***** Random Number Generators *****/
double Random(double max) {                // return -max to +max

return(max*((double)random(MAX_POS)-(double)MAX_NUM)/(double)MAX_NUM);
}

double RandomPos(double max) {              // return 0 to max
return(max*((double)random(MAX_POS))/(double)MAX_POS);
}

```

```

/***** Some Vector Utilities
*****/
DoubleVec Cross(const DoubleVec& A, const DoubleVec& B) {
    DoubleVec C(3,0.0);
    if((A.length()==3)&&(B.length()==3)) {
        C(0) = (A(1)*B(2)) - (A(2)*B(1));
        C(1) = (A(2)*B(0)) - (A(0)*B(2));
        C(2) = (A(0)*B(1)) - (A(1)*B(0));
    }
    return (C);
}

DoubleVec RandomVector(unsigned size, double max) {
    DoubleVec B(size,0.0);
    for(unsigned i=0;i<size;i++) B(i) = Random(max);
    return(B);
}

double Mag(DoubleVec V) {
    return(sqrt(dot(V,V)));
}

/***** Molecular Time Structure
*****/
struct MolTime {
    MolTime() { t=0;};
    void      Read(),
            Report();
    double    t,
            dt,
            dt2,
            max;
};

void MolTime::Read() {
    cin >> JunkText;
    cin >> dt;
    cin >> JunkText;
    cin >> max;
    dt2 = dt*dt;
}

void MolTime::Report() {

```

```

        OutputFile << "t=" << t << " dt=" << dt << " max=" << max << endl;
};

/***** Neighbor Structure
*****/
struct Radial {
    Radial();
    ~Radial();
    long      rsize;
    double    maxsize,resolution;
    void      Read(),
             Report(),
             Setup();
    DoubleVec radialdist;
};

Radial::Radial() {
    rsize=1000;
    maxsize=10.0;
}

Radial::~~Radial() {
    Report();
}

void Radial::Setup() {
    resolution=(double)rsize/maxsize;
    radialdist.resize(rsize);
}

void Radial::Report() {
    long i;
    for(i=0;i<rsize;i++)
        RadialFile <<(double)i/resolution << S
        << radialdist[i] << endl;
}

void Radial::Read() {
    cin >> JunkText;
    cin >> rsize;
    cin >> JunkText;
    cin >> maxsize;
}

```



```

struct Neighbor {
    Neighbor();
    ~Neighbor();
    long      resolution;
    void      Read(),
             Report(),
             Setup(int);
    DoubleGenMat d,
             distribution;
    double      maxsize,
             nearest,
             shellsizes;
};

Neighbor::Neighbor() {
    nearest=0.0;
    shellsizes=3.0;
    maxsize=10.0;
    resolution=100;
}

Neighbor::~~Neighbor() {
    Report();
}

void Neighbor::Setup(int num) {
    d.resize(num,num);
    distribution.resize(resolution,num);
}

void Neighbor::Report() {
    NeighborFile << "nearest=" << nearest << " shellsizes=" << shellsizes
    << " maxsize=" << maxsize << endl
    << "distribution" << endl << distribution << endl;
}

void Neighbor::Read() {
    cin >> JunkText;
    cin >> resolution;
    cin >> JunkText;
    cin >> shellsizes;
    cin >> JunkText;
    cin >> maxsize;
}

```

```

}

/***** Energy Structure
*****/
struct Energy {
    Energy() {K=V=E=D=0.0;};
    ~Energy() { Report();};
    void      Read(),
             Report();
    double    K,           // kinetic energy
             V,           // potential
             E,           // total energy
             D;           // Dissipation
};

void Energy::Report() {
    OutputFile << "K=" << K << " V=" << V << " E=" << E << endl;
}

void Energy::Read() {
    cin >> JunkText;
    cin >> K;
    cin >> JunkText;
    cin >> D;
}

/***** Temperature Class
*****/
struct Temperature {
    Temperature();
    void      Read(),
             Report();
    Statistical Real,
             Diff;
    long      steps,
             maxsteps;
    double    q,
             Zeta,
             dZeta;
};

Temperature::Temperature() {
    maxsteps=steps=0;

```

```

    q=Zeta=dZeta=0.0;
}

void Temperature::Report() {
    OutputFile << "q=" << q << " steps=" << steps << " maxsteps=" <<
    maxsteps << " Zeta=" << Zeta << " dZeta=" << dZeta << endl;
    Real.Report("Real Temp");
    Diff.Report("Diff Temp");
    cout << endl;
}

void Temperature::Read() {
    cin >> JunkText;
    cin >> Real.Set;
    if(Real.Set==0.0) return;
    cin >> JunkText;
    cin >> q;
    cin >> JunkText;
    cin >> Real.Size;
    cin >> JunkText;
    cin >> Diff.ATol;
    cin >> JunkText;
    cin >> Diff.STol;
    Diff.Size=Real.Size;
    Diff.Data.resize(Diff.Size);
    Real.Data.resize(Real.Size);
    maxsteps = (Real.Size>Diff.Size)? Real.Size: Diff.Size;
}

/***** Atom Structure
*****/
struct Atom {
    Atom();
    ~Atom()    { Report();};
    void      Report(),
             Read();

    Energy      energy;
    Element     element;
    double      m,                // mass
             KineticEnergy();

    DoubleVec   f,                // force
             p,                  // momentum
             r;                  // position
}

```

```

        int            charge,
                        num,
                        state,
                        status;
        char            name[20];
};

Atom::Atom() {
    m=0.0;
    f.resize(3);
    p.resize(3);
    r.resize(3);
    f=p=r=VectorZero;
    charge=num=state=status=0;
    strcpy(name,"\0");
}

double Atom::KineticEnergy() {
    energy.E = dot(p,p);
    energy.E /= (2.0 * m);
    return(energy.E);
}

void Atom::Read() {
    ConfigFile >> name;
    ConfigFile >> r;
    ConfigFile >> p;
    ConfigFile >> m;
    element.Assign(name);
}

void Atom::Report() {
    OutputFile << name << " ["<< r(0) << S << r(1) << S << r(2) <<
        "]" ["<< p(0) << S << p(1) << S << p(2) << "]" "<< m;
}

/***** Molecule Structure
*****/
struct Molecule {
    Potential      ms,                // metal-solvent potential
                  ss;                // solvent-solvent potential

    MolTime        time;
    Neighbor        neighbors;
};

```

```

Radial      radial;
Temperature temp;           // various Tempertature vars
Atom        *atom;         // atoms in molecule
Energy      energy,        // various energy variables
            excitation;    // excitation energy
int         atoms,        // number of atoms in molecule
            charge,        // charge on molecule
            dissociated,   // the status of the molecule
            trajectories;
double      DegreesFreedom, // degrees of freedom
            M,             // mass of molecule
            Mass(),        // calculate total mass
            KineticTemp(), // calculate the kinetic Temp
            KineticEnergy(), // calculate total K
            PotentialEnergy(), // calculate total V
            TotalEnergy();  // calculate total E
DoubleVec    CoM,          // center of mass
            CenterOfMass(), // calculate center of mass
            J,             // angular momentum
            AngularMomentum(), // calculate angular momentum
            P,            // momentum
            Momentum(),    // calculate momentum
            R,            // position
            Position();    // calculate position
DoubleGenMat I,           // moment of inertia
            MomentOfInertia(); // calculate moment of inertia
void         DampMomenta(), // remove energy by friction
            Excite(),       // impart Kinetic Energy
            Move(),         // move atoms dt in time
            Force(),        // calculate force on atoms
            Impulse(),      // calculate impulse on atoms
            EquilibrateTemp(), // get to Temp within tau
            ExtraImpulse(),  // add force keep <KE> const
            ReadConfig(),
            Trajectory(),    // do the Trajectory
            Test(int),      // test output
            Read(),         // read data
            Recalc(),       // recalculate variables
            Status(),       // like Write but more detail
            Report();       // Report about the molecule
int          Distribution();

Molecule(); // Constructor

```



```

    ~Molecule();                                // Destructor
};

/***** Molecule Member Functions
*****/
Molecule::Molecule() {
    charge=1;
    M=0.0;
    P.resize(3);
    R.resize(3);
    CoM.resize(3);
    J.resize(3);
    I.resize(3,3);
}

Molecule::~Molecule() {
    Recalc();
    Report();
}

void Molecule::Read() {
    ms.Read();
    ss.Read();
    time.Read();
    temp.Read();
    if(temp.Real.Set==0.0) excitation.Read();
    ReadConfig();
    cin >> JunkText;
    cin >> trajectories;
    DegreesFreedom = (atoms>2) ? (3.0*(double)atoms-6.0) : 1.0;
    neighbors.Read();
    neighbors.Setup(atoms);
    radial.Read();
    radial.Setup();
    Recalc();
    Report();
}

void Molecule::ReadConfig() {
    int    size;
    ConfigFile.open(ConfigName,ios::in);
    ConfigFile >> size;
    if(atoms!=size) {

```

```

        atoms = size;
        atom = new Atom[atoms];
    }
    for(int i=0;i<atoms;i++) atom[i].Read();
    ConfigFile.close();
}

DoubleVec Molecule::Momentum() {
    P=VectorZero;
    for(int i=0;i<atoms;++i) P += atom[i].p;
    return (P);
}

DoubleVec Molecule::Position() {
    R=VectorZero;
    for(int i=0;i<atoms;++i) R += atom[i].r;
    return (R);
}

double Molecule::Mass() {
    M=0.0;
    for(int i=0;i<atoms;++i) M += atom[i].m;
    return(M);
}

DoubleVec Molecule::AngularMomentum() {
    J=VectorZero;
    for(int i=0;i<atoms;i++) J += Cross(atom[i].r, atom[i].p);
    return(J);
}

Double Molecule::KineticEnergy() {
    energy.K=0.0;
    for(int i=0;i<atoms;++i) energy.K += atom[i].KineticEnergy();
    return(energy.K);
}

double Molecule::PotentialEnergy() {
    DoubleVec r(3,0.0);
    double d;

    energy.V=0.0;
    for(int i=0;i<atoms;++i)

```

```

        for(int j=i+1;j<atoms;++j) {
            r = atom[i].r - atom[j].r;
            d = Mag(r);
            energy.V += (i==0) ? ms.U(d) : ss.U(d);
        }
    return(energy.V);
}

double Molecule::TotalEnergy() {
    energy.E = PotentialEnergy() + KineticEnergy();
    return(energy.E);
}

DoubleVec Molecule::CenterOfMass() {
    CoM = VectorZero;
    for(int i=0;i<atoms;i++) CoM += atom[i].r * atom[i].m;
    CoM /= Mass();
    return DoubleVec(CoM);
}

DoubleGenMat Molecule::MomentOfInertia() {
    unsigned    j,k;

    I=MatrixZero;
    for(int i=0;i<atoms;i++) {
        I(0,0) += atom[i].m*((atom[i].r(1)*atom[i].r(1))+
            (atom[i].r(2)*atom[i].r(2)));
        I(1,1) += atom[i].m*((atom[i].r(0)*atom[i].r(0))+
            (atom[i].r(2)*atom[i].r(2)));
        I(2,2) += atom[i].m*((atom[i].r(0)*atom[i].r(0))+
            (atom[i].r(1)*atom[i].r(1)));
        for(j=0;j<3;j++)
            for(k=0;k<3;k++)
                if(j!=k) I(j,k) -=
                    atom[i].m*atom[i].r(j)*atom[i].r(k);
    }
    return(I);
}

void Molecule::Excite() {
    int i;
    double scalepop;
    DoubleVec w(3,0.0), LinearP(3,0.0);

```

```

    if(CenterOfMass()!=VectorZero)
        for(i=0;i<atoms;i++)
            atom[i].r -= CoM;
    for(i=0;i<atoms;++i)
        atom[i].p = RandomVector(3,excitation.K);
    w = solve(MomentOfInertia(),AngularMomentum());
    for(i=0;i<atoms;++i)
        atom[i].p -= Cross(w,atom[i].r) * atom[i].m;
    LinearP = Momentum()/M;
    for(i=0;i<atoms;i++)
        atom[i].p -= LinearP * atom[i].m;
    scalepop = sqrt(excitation.K/KineticEnergy());
    for(i=0;i<atoms;i++)
        atom[i].p *= scalepop;
    Recalc();
}

void Molecule::Force() {
    DoubleVec    force(3,0.0);

    for(int i=0;i<atoms;i++) atom[i].f=VectorZero;
    for(i=0;i<atoms;i++)
        for(int j=i+1;j<atoms;j++) {
            force = atom[j].r - atom[i].r;
            neighbors.d(i,j) = Mag(force);
            force *= (i==0) ?
                ms.gU(neighbors.d(i,j))/neighbors.d(i,j):
                ss.gU(neighbors.d(i,j))/neighbors.d(i,j);
            atom[i].f += force;
            atom[j].f -= force;
        }
}

void Molecule::Impulse() {
    Force();
    for(int i=0;i<atoms;i++) atom[i].p += atom[i].f * time.dt;
}

void Molecule::ExtraImpulse() {
    temp.dZeta = Kb_AmuAps*(DegreesFreedom+1.0)*(temp.Diff.Val)/temp.q;
    temp.Zeta += temp.dZeta * time.dt;
    for(int i=0;i<atoms;i++)
        atom[i].p -= temp.Zeta * atom[i].p * time.dt;
}

```

```

}

double Molecule::KineticTemp() {
    double dummy =0.0;
    for(int i=0;i<atoms;i++)
        dummy += dot(atom[i].p,atom[i].p)/atom[i].m;
    dummy /= (Kb_AmuAps*DegreesFreedom);
    return(dummy);
}

int Molecule::Distribution() {
    int i,j,dum,n1=0;
    long dummy=0;

    dum = floor(((double)neighbors.resolution*(time.t/time.max)));
    if(dum>=neighbors.resolution) dum = (neighbors.resolution - 1);
    neighbors.distribution(dum,0)++;
    for(i=1;i<atoms;i++) {
        if(neighbors.d(0,i)<neighbors.shellsizesize) n1++;
        if(neighbors.d(0,i)>neighbors.maxsize)
            dissociated=i;
        if(neighbors.d(0,i)<radial.maxsize) {
            dummy=(long)(neighbors.d(0,i)*radial.resolution);
            radial.radialdist[dummy]+=1.0;
        }
    }
    neighbors.distribution(dum,n1)++;
    return(dissociated);
}

void Molecule::DampMomenta() {
    for(int i=0;i<atoms;i++)
        atom[i].p *= excitation.D;
}

void Molecule::Move() {
    for(int i=0;i<atoms;i++) atom[i].r += atom[i].p * time.dt / atom[i].m;
}

void Molecule::EquilibrateTemp() {
    int fillarray=0,firsttime=1;
    double top=0.0,bottom=0.0;

```



```

time.t=0.0;
for(int i=0;i<atoms;i++) {
    top += dot(atom[i].p,atom[i].f);
    bottom += Mag(atom[i].p);
}
temp.Zeta = top/bottom;
do {
    time.t += time.dt;
    temp.steps++;
    Impulse();

    temp.Real.Val = KineticTemp();
    temp.Real.Data(temp.steps) = temp.Real.Val;
    temp.Real.Var = variance(temp.Real.Data);
    temp.Real.Avg = mean(temp.Real.Data);
    temp.Real.Std = sqrt(temp.Real.Var);

    temp.Diff.Val = temp.Real.Val - temp.Real.Set;
    temp.Diff.Data(temp.steps) = temp.Diff.Val;
    temp.Diff.Var = variance(temp.Diff.Data);
    temp.Diff.Avg = mean(temp.Diff.Data);
    temp.Diff.Std = sqrt(temp.Diff.Var);

    ExtraImpulse();
    Move();
    temp.steps%=temp.maxsteps;
    if(!temp.steps) fillarray=1;
    if (TESTING) Test(firsttime);
    if(firsttime) firsttime=0;
} while( (fabs(temp.Diff.Avg) > temp.Diff.ATol)
        || (fabs(temp.Diff.Std) > temp.Diff.STol) || !fillarray );
}

void Molecule::Trajectory() {
    trajectories--;
    dissociated=0;
    time.t=0.0; // time zero
    do {
        dissociated=Distribution();
        time.t += time.dt; // step time
        Impulse(); // change momenta
        if (excitation.D!=0.0)
            DampMomenta(); // slow atoms down
    }
}

```

```

        if (temp.Real.Set!=0.0) {
            temp.Real.Val = KineticTemp();
            temp.Diff.Val = temp.Real.Val - temp.Real.Set;
            ExtraImpulse();           // for constant <KE>
        }
        Move();                      // move atoms
        if (TESTING) Test(0);
    } while((time.t<time.max)&&(!dissociated));
    if(!trajectories) {
        neighbors.Report();
        radial.Report();
    }
    Report();
}

void Molecule::Test(int one) {
    static int lines;
    if(!lines&&one) {
        Report();
        printf("%s\t%s\t%s\t%s\t%s\t%s\t%s\t%s\n",
            "t", "KE", "V", "T", "a(T-To)", "s(T-To)", "Z", "dZ");
    }
    printf("%g %g %g %g %g %g %g %g\n",
        time.t, KineticEnergy(), PotentialEnergy(), temp.Real.Val,
        temp.Diff.Avg, temp.Diff.Std, temp.Zeta, temp.dZeta );
    if(one) {
        lines++;
        lines%=24;
    }
}

void Molecule::Recalc() {
    Mass();
    Momentum();
    AngularMomentum();
    MomentOfInertia();
    CenterOfMass();
    KineticEnergy();
    PotentialEnergy();
    TotalEnergy();
    KineticTemp();
    Force();
}

```

```

void Molecule::Status() {
    Report();
    OutputFile << "M=" << M << endl
        << "P= [" << P(0) << S << P(1) << S << P(2) << "]" << endl
        << "J= [" << J(0) << S << J(1) << S << J(2) << "]" << endl
        << "CoM= [" << CoM(0) << S << CoM(1) << S << CoM(2) << "]"
        << endl << "I= " << I << endl;
}

```

```

void Molecule::Report() {
    Recalc();
    time.Report();
    energy.Report();
    if(temp.Real.Set>0) temp.Report();
    OutputFile << atoms << endl;
    for(int i=0;i<atoms;i++) {
        atom[i].Report();
        OutputFile << S << neighbors.d(0,i) << endl;
    }
}

```

/****** Main Program

*****/

```

int main() {
    long trajs;
    printf("\n%s\n",BANNER);
    printf("\nStarted at: %s\n",timestamp());
    Molecule mol;

    cin >> ConfigName;
    cin >> NeighborName;
    cin >> RadialName;
    cin >> LogName;
    cin >> OutputName;

    LogFile.open(LogName,ios::out);
    NeighborFile.open(NeighborName,ios::out);
    RadialFile.open(RadialName,ios::out);
    OutputFile.open(OutputName,ios::out);

    mol.Read();
    if (mol.trajectories == -1) mol.trajectories = TESTING = 1;
    do {

```

```

    if(mol.temp.Real.Set!=0.0) mol.excitation.K=
        mol.DegreesFreedom*mol.temp.Real.Set*Kb_AmuAps/2.0;

    if(mol.excitation.K !=0.0) {
        LogFile << "Excite" << endl;
        mol.Excite();
    }

    if(mol.temp.Real.Set!=0.0) {
        LogFile <<"Equilibrate" << endl;;
        mol.EquilibrateTemp();
    }

    LogFile << "Trajectories Remaining "
        << mol.trajectories << endl;
    cout << "Trajectories Remaining "
        << mol.trajectories << endl;
    mol.Trajectory();
    mol.ReadConfig();
} while(mol.trajectories>0);

LogFile.close();
NeighborFile.close();
RadialFile.close();
OutputFile.close();

printf("\nStopped at: %s\n",timestamp());
return(0);
}

```

Kinetic Rate Fitting Code

```

/* C++ Program to fit classical trajectory data from Var6+ isomerization either canonical
 * or microcanonical.
 *
 * Program compiles under OS/2 IBM's CSet++ 2.1.
 *
 * Program Name:    <k22fit6.cpp> Ver 1.6 for C++
 * Author:         Robert L. Asher
 * Employer:       University of Florida / Philip J. Brucat
 * Original Date:   May 1, 1994
 * Revision Date:   July 1, 1994
 *
 */

```

```

/***** Standard C++ Include Files
 *****/

```

```

#include <conio.h>           // C++ console routines
#include <ctype.h>           // C++ types
#include <fcntl.h>           // C++
#include <float.h>           // C++ floating point routines
#include <math.h>            // C++ math routines
#include <stddef.h>          // C++ standard definitions
#include <stdio.h>           // C++ standard I/O routines
#include <stdlib.h>          // C++ standard library
#include <stdarg.h>          // C++ standard argument
#include <string.h>          // C++ string routines
#include <iostream.h>        // C++ I/O stream routines
#include <fstream.h>         // C++ file I/O stream
#include <time.h>            // C++ time classes
#include <limits.h>

```

```

double t[1000],Conc[3][1000],Calc[3][1000],Traj[7][1000];

```

```

double timestart, dt, k[4], timelimit,
       lambda2, lambda3, dummy,
       lam2_3, lam22_3, lam32_3, lam23,
       A0=1,
       A[3][3],
       kcrit,
       accept_value,
       kstep[4],
       p,p2,q,ts;

```



```
char    guano[80],NNfile[80],Parfile[80],Fitfile[80],Text[80][80];
```

```
long    NNsize, timenum, i, j, itterations, temp;
```

```
int     ii,itt,Out;
```

```
int ReadData(char Filename[]) {
```

```
    int error=0;
```

```
    ifstream IN(Filename);
```

```
    if(!IN) error=1;
```

```
    else {
```

```
        for(i=0;i<6;i++) IN >> guano;
```

```
        for(j=0;j<1000;j++) for(i=0;i<7;i++) IN >> Traj[i][j];
```

```
        IN.close();
```

```
    }
```

```
    return(error);
```

```
}
```

```
int ReadPar(char Filename[]) {
```

```
    int error=0;
```

```
    ifstream IN(Filename);
```

```
    if(!IN) error=1;
```

```
    else {
```

```
        i=0;
```

```
        do {
```

```
            IN >> Text[i];
```

```
            i++;
```

```
        } while (!IN.eof());
```

```
        IN.close();
```

```
    }
```

```
    if(i<58) {
```

```
        cout << "pop\n";
```

```
        temp=0;
```

```
        strcpy(NNfile,Text[1]);
```

```
        dt=(double)atof(Text[11]);
```

```
        timelimit=(double)atof(Text[13]);
```

```
        NNsize=atol(Text[23]);
```

```
        k[0]=(double)atof(Text[29]);
```

```
        k[1]=(double)atof(Text[32]);
```

```
        k[2]=(double)atof(Text[35]);
```

```
        k[3]=(double)atof(Text[38]);
```

```
        kstep[0]=(double)atof(Text[30]);
```

```
        kstep[1]=(double)atof(Text[33]);
```

```
        kstep[2]=(double)atof(Text[36]);
```

```

        kstep[3]=(double)atof(Text[39]);
        kcrit=(double)atof(Text[41]);
        timestart=(double)atof(Text[43]);
        itterations=(double)atof(Text[45]);
        Out=atoi(Text[47]);
    } else {
        cout << "temp\n";
        temp=4;
        strcpy(NNfile, Text[1]);
        dt=(double)atof(Text[11]);
        timelimit=(double)atof(Text[13]);
        NNsize=atol(Text[27]);
        k[0]=(double)atof(Text[33]);
        k[1]=(double)atof(Text[36]);
        k[2]=(double)atof(Text[39]);
        k[3]=(double)atof(Text[42]);
        kstep[0]=(double)atof(Text[34]);
        kstep[1]=(double)atof(Text[37]);
        kstep[2]=(double)atof(Text[40]);
        kstep[3]=(double)atof(Text[43]);
        kcrit=(double)atof(Text[45]);
        timestart=(double)atof(Text[47]);
        itterations=(double)atof(Text[49]);
        Out=atoi(Text[51]);
    }
    return(error);
}

void PrintData() {
    for(j=0;j<1000;j++) {
        for(i=0;i<7;i++) cout << Traj[i][j] << " ";
        cout << "\n";
    }
}

void Concentration() {
    for(i=0;i<3;i++) for(j=0;j<1000;j++)
        Conc[i][j]=(Traj[6-i][j]-1e-4)/Traj[0][j];
}

double LeastSquaresRates(double K[]) {
    double sum, dummy;

```

```

p=K[0]+K[1]+K[2]+K[3];
p2 = p*p;
q=sqrt(p2 -4.0*(K[0]*K[2]+K[1]*K[3]+K[0]*K[3]));
lambda2=(p+q)/2.0;
lambda3=(p-q)/2.0;
lam23=lambda2*lambda3;
lam2_3=lambda2-lambda3;
lam22_3=lambda2*lam2_3;
lam32_3=lambda3*lam2_3;
A[0][0]=K[1]*K[3]/lam23;
A[1][0]=K[0]*K[3]/lam23;
A[2][0]=K[0]*K[2]/lam23;
A[0][1]=K[0]*(lambda2 - K[2] - K[3])/lam22_3;
A[1][1]=K[0]*(K[3] - lambda2)/lam22_3;
A[2][1]=K[0]*K[2]/lam22_3;
A[0][2]=K[0]*(K[2] + K[3] - lambda3)/lam32_3;
A[1][2]=K[0]*(lambda3 - K[3])/lam32_3;
A[2][2]=-K[0]*K[2]/lam32_3;

for(i=0;i<3;i++) for(j=0;j<1000;j++)
    Calc[i][j]= A0*(A[i][0] + A[i][1]*exp(-lambda2*t[j]) +
        A[i][2]*exp(-lambda3*t[j]));
for(j=timenum;j<1000;j++) for(i=0;i<3;i++) {
    dummy =(Conc[i][j]-Calc[i][j]);
    sum+=dummy*dummy;
}
return(sum);
}

double Minimizer(double (*Mname)(double*), double start[],
    double initstep[], double crit, int num, int it) {
    double test,
        value,
        *guess= new double[num],
        *step= new double[num],
        oldvalue=Mname(start),
        abscrit=fabs(crit),
        divisor=-2.0 + abscrit;
    int done=0;
    for(i=0;i<num;i++) {
        guess[i]=start[i];
        step[i]=initstep[i]*guess[i];
    }

```

```

do {
    guess[it] += step[it];
    value = Mname(guess);
    if (value > oldvalue) step[it] /= divisor;
    test = value - oldvalue;
    if (fabs(test) < abscrit) done=1;
    else oldvalue = value;
} while (!done);
return(guess[it]);
}

void ConcentrationData() {
    for(j=0;j<1000;j++) {
        for(i=0;i<3;i++) cout << Calc[i][j] << " ";
        for(i=0;i<3;i++) cout << Conc[i][j] << " ";
        cout << "\n";
    }
}

int WritePar(char Filename[]) {
    int error=0;
    ofstream OUT(Filename);
    if(!OUT) error=1;
    else {
        for(i=0;i<4;i++) OUT << Text[i] << "\n";
        for(i=4;i<10;i+=3)
            OUT << Text[i] << " " << Text[i+1] << " "
                << Text[i+2] << "\n";
        for(i=10;i<28+temp;i+=2)
            OUT << Text[i] << " " << Text[i+1] << "\n";
        OUT << "k12: " << k[0] << " " << kstep[0] << "\n";
        OUT << "k21: " << k[1] << " " << kstep[1] << "\n";
        OUT << "k23: " << k[2] << " " << kstep[2] << "\n";
        OUT << "k32: " << k[3] << " " << kstep[3] << "\n";
        OUT << "kcrit: " << kcrit << "\n";
        OUT << "timestart: " << timestart << "\n";
        OUT << "ititerations: " << ititerations << "\n";
        OUT << "output: " << Out << "\n";
        OUT << "LeastSquaresRates= " << LeastSquaresRates(k) << "\n";
        OUT << "From t= " << t[timenum] <<
            " to " << t[NNsize-1] << "\n";

        OUT.close();
    }
}

```

```

    }
    return(error);
}

int main(int argc, char **argv) {
    if (argc>1) {
        strcpy(Parfile,argv[1]);
        if (argc>2) strcpy(Fitfile,argv[2]);
        else strcpy (Fitfile,"guano.fit");

        ReadPar(Parfile);

        ts = timelimit/(double)NNsize;
        for(i=0;i<NNsize;i++) t[i]=(double)i*ts;
        timenum=floor(timestart/ts);

        ReadData(NNfile);                //      PrintData();
        Concentration();

        for(itt=0;itt<ititerations;itt++) {
            ii=rand()%4;
            k[ii]=Minimizer(LeastSquaresRates,k,kstep,kcrit,4,ii);
            WritePar(Fitfile);
        }

        if(Out) ConcentrationData();
    }
    return(0);
}

```


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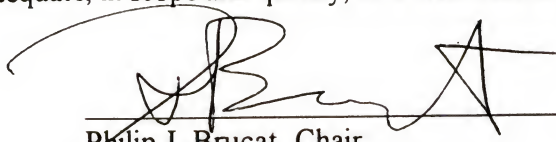
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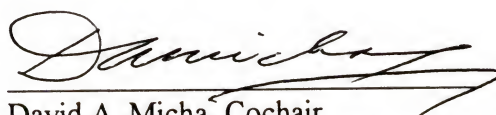
BIOGRAPHICAL SKETCH

The author was born at 10:45 pm on November 9, 1964 to Rev. William Lee Asher, Jr., and Charlotte Kane Asher (now Charlotte Kane Kurtz) in Norfolk, Virginia. In the Spring of 1983, he graduated from Charles D. Owen High School, located in the beautiful Swannannoa Valley of Western North Carolina. He entered the University of North Carolina Asheville in the fall of that same year. Five years later, in the Summer of 1988, he received a Bachelor of Science degree majoring in chemistry and physics. He proceeded directly to the University of Florida in the Fall of 1988. As a graduate student in the physical chemistry division he continued his pursuit of physics and chemistry. In the Spring of 1989 he joined Philip J. Brucat's experimental research group and David A. Micha's theoretical group to investigate small molecular ions in hopes of gaining insight utilizing their various approaches. On December 31, 1993, he was married to Sandra Lynn Crowell. On November 27, 1994 at 8:27 pm Robert and Sandra were blessed with a son, Trebor Lee Asher, to give them clearer perspective.

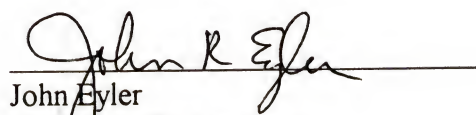
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Philip J. Brucat, Chair
Associate Professor of Chemistry

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David A. Micha, Cochair
Professor of Chemistry and Physics

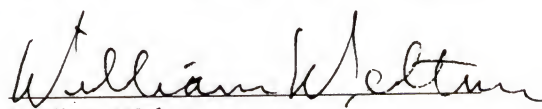
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John Eyer
Professor of Chemistry

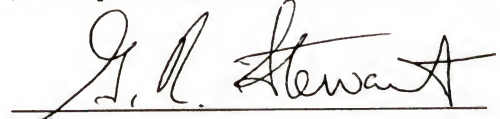
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Martin Vala
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


William Weltner
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

A handwritten signature in dark ink, appearing to read "G. M. Stewart", is written over a horizontal line.

Gregory Stewart
Professor of Physics

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1995

Dean, Graduate School